The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

Cellulose Fiber-to-Fiber and Fines-to-Fiber Interactions: Their Coagulation and Flocculation Tendencies as Affected by Electrolytes and Polymers in an Agitated Water Slurry

C. A. (Kasy) King

January, 1975

CELLULOSE FIBER-TO-FIBER AND FINES-TO-FIBER INTERACTIONS: THEIR COAGULATION AND FLOCCULATION TENDENCIES AS AFFECTED BY ELECTROLYTES AND POLYMERS IN AN AGITATED WATER SLURRY

A thesis submitted by

C. A. (Kasy) King

B.S. Chem. 1970, Virginia Polytechnic Institute and State University

M.S. Chem. 1972, Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements
of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence University,
Appleton, Wisconsin

January, 1975

This Thesis is Dedicated to my Wife, Donna

and my Sons, Todd and Mark

TABLE OF CONTENTS

SUMMARY

Cellulose fines-to-fiber and fiber-to-fiber interactions have been compared on the basis of their coagulation and/or flocculation tendencies as affected by simple electrolytes, polyelectrolytes, pH, agitation, and fines addition.

Results indicated that the two test systems interacted in the same way under the influence of simple electrolytes, with the electrolyte concentration required to completely coagulate fines-to-fiber and fiber-to-fiber systems being the same. It was demonstrated that La(+3) was a better coagulant than Ca(+2) than was Na(+1) as predicted qualitatively by the DLVO theory (1-4).

Polymer effects were such that it was possible to have both fiber dispersion and fines retention at the same polymer concentration, indicating the possibility of obtaining excellent sheet formation and good cellulose material retention at the same time in mill situations. The cationic polyacrylamide flocculant was more effective on both fiber-to-fiber and fines-to-fiber systems than was either the anionic or nonionic polyacrylamide.

It was found that pH changes over the range of pH 5 to pH 9 had no effect on fiber-to-fiber interactions with polymers, but did affect fines-to-fiber interactions with polymers. These pH effects in general followed the charge requirements of the functional groups of the polymers. The cationic test polymer at pH 5 was more effective in increasing fines-to-fiber interactions than at pH 9. More tertiary amine groups of the polymer were positively charged at pH 5 than 9; thus the polymer interacted more strongly with the negatively charged cellulose under acidic conditions compared to basic conditions.

Changes in agitation had no effect on the action of simple electrolytes, but did show a pronounced effect on polymer systems. Agitation affected polymer systems in both the fiber-to-fiber and fines-to-fiber cases. For the fiber-to-fiber systems, when strong polymer-fiber interactions were present, less polymer was required to reach maximum flocculation at elevated agitations. The implication being that the increased particle collision frequency and kinetic energy resulting on increased agitation made it easier for the polymer to bridge particles together and more difficult for the forces of turbulence to disrupt fiber-polymer interactions. For systems of weak fiber-polymer interactions, no fiber flocculation was observed at elevated agitation, indicating that the forces of turbulence were intense enough to disrupt fiber-polymer bridges. In general, the fines-to-fiber interactions as affected by polymer additives followed the same agitation tendencies as explained above for the fiber-to-fiber systems.

Results indicated that the level of fines addition affected the degree of fiber flocculation. A 10% fines level based on fiber weight was flocculated more completely by the cationic polymer than at a 1% level. This result has been interpreted as an extension of the polymer chain length as a result of the fines addition. Without the fines, or at low fines levels, the bridged structure is mainly fiber — polymer — fiber in nature, but with the increased fines level, it becomes possible to extend the polymer bridge. The extended bridge structure, fiber — polymer — fines — polymer — fiber, permits the elongated polymer chains to become better flocculating agents, by stretching into the liquid medium to a greater length and attaching to individual fibers more readily.

INTRODUCTION

GENERAL

There are two interacting cellulosic systems of importance in the papermaking process, the fiber-to-fiber and the fines-to-fiber systems. The extent to which fibers and fines interact greatly affects certain processes, such as sheet forming and fines retaining (5-19).

The fiber weight distribution observed in a finished sheet of paper is very much dependent on the fiber distribution in the pulp slurry prior to sheet formation. If the fibers were evenly distributed in the slurry prior to sheet formation, then the finished sheet would have a uniform fiber weight distribution. On the other hand, if the fiber slurry was composed of large clusters or aggregates of fibers, then the finished sheet would also have areas of high and low fiber density. This latter condition leads to a paper sheet of poor physical and optical properties.

It thus appears that a very uniform fiber slurry with completely dispersed fibers would be desired. However, this high degree of dispersion leads to a large loss of cellulosic material as the slurry is passed over the suction boxes (20,21). By having the fines of the system completely dispersed, the plugging of the fiber mat pore and of the wire openings during sheet forming is minimized. Naturally, this loss of material is an economic burden and should be minimized as much as possible.

Thus, it is apparent that one of the main papermaking challenges becomes one of finding the proper combination of raw material retention, and sheet-forming parameters in order to obtain a finished product which meets or exceeds certain preset criteria of cost, sheet strength properties, sheet optical

properties, etc. And so, it becomes important for the papermaker to realize and understand better the interacting fiber and fines systems of the pulp slurry, plus have a more complete knowledge of what controlling influences he may have over these systems.

Up to this time, there has been little distinction made between the fiber-to-fiber and fines-to-fiber systems. It has generally been held that the two systems will behave in the same way under similar conditions. For example, Strazdens (22) assumes that the surface charge is the same for both fines and fibers. Assumptions of the similarities of the systems generally come about because of the ease in measuring fines-to-fiber interactions via a mass balance technique (23-26). On the other hand, some authors (19,27) have used optical or visual techniques to study fiber-to-fiber interactions, extrapolating observed results to cover almost all systems of the wet end of the papermaking process. Das and Lomas (28) arrive at a polymer bridging mechanism for a system of fines only, and then apply their findings to a papermaking slurry without questioning fiber effects at all. However, it is becoming more and more apparent in the literature that fiber-to-fiber and fines-to-fiber interactions both have important effects on sheet properties and cannot be separated easily. Ogiwara and Kubota (29) have demonstrated that fines do show a higher fixation for filler than do fibers, while Vallette and Lafaye (30) distinguished between fines and fiber effects by comparing Dennison wax picking tests and look through tests, respectively.

The present program is the first to present a concerted effort to simultaneously study fines-to-fiber, fiber-to-fiber with fines, and fiber-to-fiber without fines interactions. It is realized that the fiber-to-fiber interactions without fines is not a realistic commercial process, since it is

never possible to completely eliminate fines from fibers. In actual mill situations fines and fibers are always both present in the fiber slurry. However, in order to determine the effects that the fines may show on fiber interactions, both fiber-to-fiber with fines and without fines will be studied.

CONTROLLING FACTORS FOR CELLULOSIC MATERIAL INTERACTIONS

At this point in the discussion, it is appropriate to define some of the terms which will be used throughout this presentation. Coagulation will be used as in the context presented by LaMer and Smellie (31) to describe a process by which the addition of simple electrolytes leads to the direct interaction and aggregation of small particles, and in particular via the mechanism of electric double layer collapse. The term flocculation as presented by LaMer and Smellie will be used in referring to a process by which long-chain polymers become attached to several small individual particles simultaneously resulting in particle cluster formation. In this presentation, coagulation and flocculation refer to specific types of particle agglomeration, while cluster formation, agglomeration, or aggregation refer to general processes of fiber-fines network formation, where either coagulation or flocculation, both, or neither process may be the cause of particle enlargement.

Dispersion or redispersion is the opposite process to particle aggomeration, i.e., particles become separated, with the destruction of fiber-fines networks. The term retention will be used in the general sense to describe the amount of material attached or bound to the cellulose pulp fibers (5).

Particle aggregation in a pulp slurry is a very intricate process, with many controlling factors acting simultaneously. The controlling factors for

cellulosic particle agglomeration can be grouped into four main divisions (32-34): (1) properties of fibers and fines, (2) consistency of slurry, (3) fluid conditions of slurry, and (4) chemical environment of system water. These divisions were most recently reviewed by Persinger (35).

PROPERTIES OF FIBERS AND FINES

The important properties of cellulose fibers and fines that influence network formation are particle thickness, width, and length; flexibility; and physical surface conditions. Physical entanglement of the cellulosic particles is an important mode of cluster formation (35-37). Overall cluster formation is governed by a balance between the factors which influence particle aggregation and factors which influence particle separation. It is generally held that the greater the length and flexibility of the particle, plus the greater the number of collisions it experiences with other particles, the greater will be the degree to which particle agglomeration will occur (36-38). On the other hand, as the disruptive forces of the system are increased, it is possible that the particles will be separated. Separation will occur if the disruptive turbulence forces are sufficient to break apart the fiber-fines network. Disruptive forces are a result of the agitation or turbulence of the slurry.

A particle's flexibility depends on its length and rigidity: the longer and less rigid is the particle, the more likely it is to form fiber-fines networks. Persinger (35) speculates that when particle thickness and rigidity do not vary greatly, the tendency to form clusters via entanglement is directly proportional to particle length.

The number of contacts that particles make with each other is important in determining the degree of aggregation (36). The more surface area that

particles have, the more points of contact for entanglement there will be. For example, a cellulose fiber exhibiting very few fibrils and of a certain length demonstrates a certain tendency toward cluster formation. At the same time, a fiber of the same length and composition, but with more fibrils as a result of beating will show an increased tendency to form fiber networks (39-42).

CONSISTENCY OF SLURRY

The influence of particle concentration on network formation is a straightforward concept. As the number of particles per unit volume is increased, the number of times a particle undergoes contact with other particles increases, resulting in an increased probability of particle entanglement. Increased concentration also causes less individual particle movement, resulting in lowered localized disruptive forces. Chiu (43) observed this effect of concentration during a flocculation study on a bleached softwood kraft pulp.

FLUID CONDITIONS OF THE SLURRY

Slurry fluid conditions of importance are viscosity (temperature), degree of agitation, and temperature. "Dynamic equilibrium" as a concept of cluster formation and disruption was first proposed by Hubley, et al. (44). This concept asserts that the agitation and turbulent conditions of a fiber slurry bring about fiber collisions resulting in cluster formation, while at the same time breaking apart previously formed aggregates. A dynamic equilibrium is established between the formation and disruption of fiber clusters, resulting in network structures somewhere between completely formed and completely destroyed. The turbulence of a particular system depends on the amount of

agitation supplied by some external mechanical means, the viscosity of the suspending medium, and the shape of the containing vessel. Walkush (4) has shown this concept to apply to fines retention, noting that retention of fines was determined by a balance between attachment and removal rates. In his work, attachment was controlled by colloidal parameters, while separation was controlled by the physical parameters affecting turbulence.

Temperature is an important parameter in the context of medium conditions, since changes in temperature result in a change of water viscosity (45). A decrease in viscosity results in an increased vortex activity, which has the effect of decreasing cluster formation.

CHEMICAL ENVIRONMENT OF SLURRY

Important conditions of the water environment include the presence of additives (either simple electrolyte or polymer), system pH, and system temperature. As stated earlier, the term retention has come to describe the amount of material bound to slurry fiber. The attached materials can be anything from fines and fiber themselves to colloidal particles such as rosin size, dyes, and TiO_2 pigments. Similarly, the term retention aid has come to imply any chemical additive placed in a papermaking slurry for the purpose of increasing the amount of materials retained in the final paper product. These retention aids are commonly in the form of simple electrolyte salts, natural polymers, or synthetic polymers. These additives alter the degree of fiber-fines network formation by changing the chemical environment about the particles involved. Some of these environmental changes will be discussed in later sections.

Although not an additive in the sense of a retention aid, air can influence particle agglomeration by attaching itself to two or more particles at

the same time as shown in (46-49), and reviewed by Swanson (12). This observation is supported by noting that when a fiber slurry is deaerated, the fiber clusters are dispersed by very gentle agitation (50).

Another way to alter the chemical environment of a papermaking slurry is to vary the pH of the water. Varying the pH can alter the surface chemical properties of cellulose materials and/or additives, thus changing their tendencies to interact with each other. For example, Walkush (5) has evaluated fines retention on pH changes over the range 1.0 to 10.0. Walkush found a decrease in retention as the pH was increased over a narrow range up to pH 4.0, observing that the hydrogen ion was probably reducing the surface charge of the fines. Walkush found no pH dependence above pH 4.0.

Temperature is an important consideration in the additive section, not because it actually alters the chemical composition, but because it can affect the energetics of the system interactions. For example, this author in earlier work demonstrated that CO_2 was sorbed by phenolic materials and silicone elastomer inversely with temperature (51). Gostkowski (52) has demonstrated that the coagulation ability of some charged ions is proportional to the mobility of the ions, noting that the ionic mobility is dependent on the temperature of the supporting medium (53).

BACKGROUND STUDIES

It is generally accepted that there are three mechanisms by which particle interactions may be increased in a papermaking system: (1) collapse and/or compression of the diffuse electric double layer surrounding the particles by the addition of electrolyte salts, (2) particle bridging by the action of long-chain synthetic or natural polymers, and (3) mechanical

entanglement of individual particles with other particles. There is also the possibility of a combination of the above three mechanisms as a means of particle agglomeration. Several studies have been conducted in the above areas, with a brief review of them given in the following paragraphs. Other subjects to be discussed in the remainder of this introductory section include a review of the principal studies from which this work was derived, and a review of previous studies employing the fiber optics light probe, which was the major experimental tool used for this study.

ELECTRIC DOUBLE LAYER CONSIDERATIONS

The electric double layer effects arise from the fact that solids suspended in a liquid medium can become electrically charged at the solid-liquid interface. The charge at the solid surface carries with it an opposite or countercharge extending a finite distance out into the liquid phase. These diffuse charges of the liquid phase prevent particles from approaching each other closely enough for the Van der Waals attractive forces to hold the particles together. The degree of particle separation then becomes a function of the extent to which the diffuse countercharge extends outward from the particle.

The surface charge of the solid surface is acquired either by direct ionization of constituent groups or by adsorption of specific ionic species. It is generally accepted that the surface charge of cellulose is negative as illustrated in Fig. 1 and reviewed by Walkush (5), with the first supportive evidence for negatively charged cellulose being given by Perrin (54). However, it is not generally known exactly how cellulose acquires its charge (55).

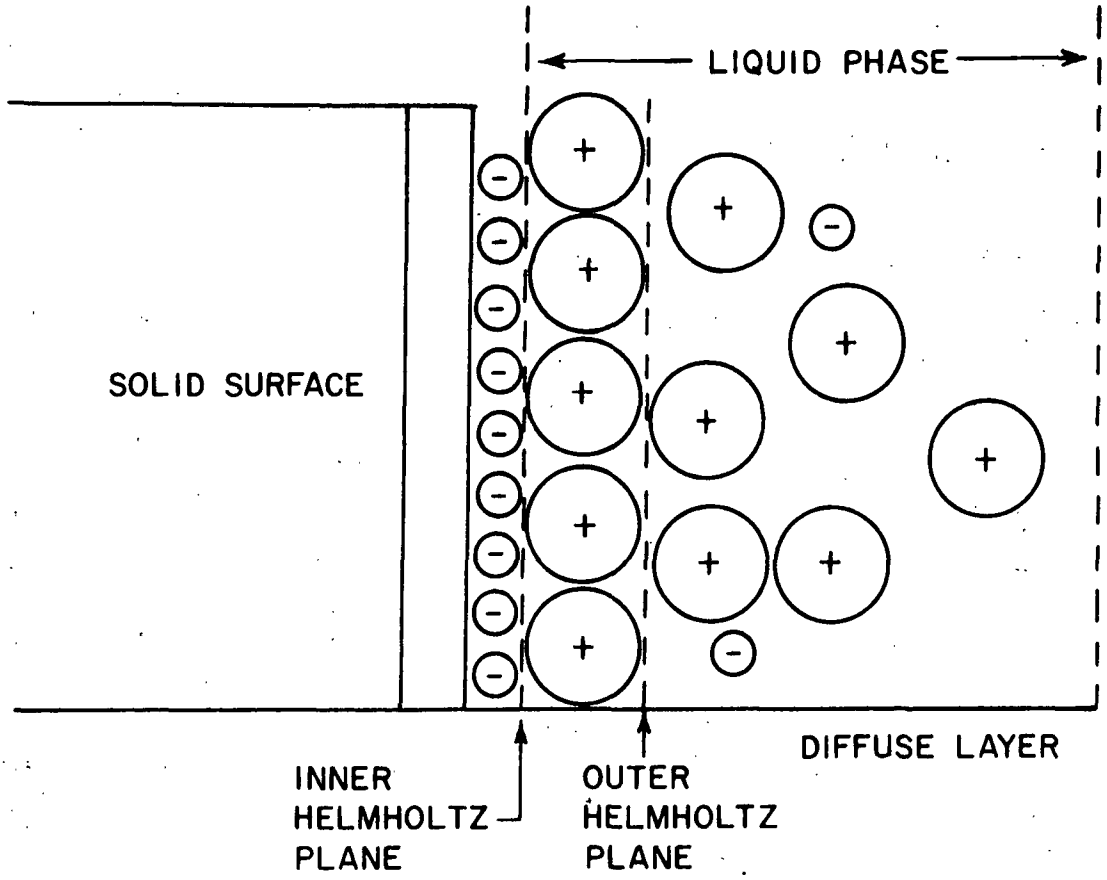


Figure 1. Representation of Cellulose Electric Double Layer

The first quantitative theoretical explanation of the double layer was given by Helmholtz (56) depicting a very thin double layer with rigidly bound ions to the solid surface. Gouy (57) and Chapman (58) pointed out almost simultaneously that an excess of similarly charged ions could not be wholly concentrated at the interface, because thermal motion will not allow the ions to remain stationary. Thus, a diffuse layer of ions is established with a potential drop from the solid surface into the bulk solution. Stern (59) was the first to modify the existing model by proposing a layer of strongly held and immobile counterions next to the solid surface. The "Stern layer" has a thickness on the order of a few ionic diameters and does not completely neutralize the surface charge. The surface charge is completely neutralized by the remaining ions of the diffuse layer in the liquid phase. The potential

of the diffuse layer ions decays exponentially with distance from the solid surface. A much more complete review of electric double layer theory can be found elsewhere as, for example, by Sheludko (60).

Adamson (61) has reviewed the parameters which can affect the extent of influence of the diffuse layer. The greater the electrolyte concentration in the liquid phase, the more ions that are available to neutralize the surface charge of the solid, thus reducing the double layer effect. Williams and Swanson (62) have demonstrated one effect of electrolyte concentration by showing that the maximum interaction of titanium dioxide particles with pulp fiber occurs at electrolyte concentrations where the double layer was essentially completely compressed. The works of Wollwage (27), Beasley (63), and Erspamer (64) have shown that varying the electrolyte concentration alters the coagulation tendencies of cellulose fibers, but only for low shear rates and low pulp consistencies. Walkush (5) has shown that carbon-14 radioactively tagged fines are retained to the greatest extent at a point of minimum electric double layer influence.

The size and valence of the ionic species in solution are also important factors affecting the extent of double layer influence. The greater the valence of the counterion, the fewer ions that are required to neutralize the solid surface charge. This fact is in compliance with the Schulze-Hardy rule, which predicts that the concentration required to compress the electric double layer decreases as the inverse sixth power of valence. Walkush (5) has shown that La(+3) is a better fines retention aid than is Ca(+2) than is Na(+1).

The charge density of an ion will affect its ability to compress an electric double layer. Ions of high charge density (either small in size or high in charge) will act as a nucleus for clusters of structured water via

an ion-dipole interaction (65). With ions of low valence or large size, the opposite tendency is present. The former group of ions is considered to be a solvent "structure maker," while the latter group is considered to be a solvent "structure breaker." Cellulose, a structure breaker (66), will be surrounded by a solvation sheath which is relatively impervious to solutes with weak electronic fields, i.e., structure breakers. On the other hand, strong coulombic fields or structure makers will be able to penetrate the cellulose solvent layer and adsorb onto the cellulose surface. Thus, structure makers can more easily alter the double layer about cellulose than can structure breakers.

It would be expected that changes in pH at a constant electrolyte background concentration can also influence the extent of double layer effectiveness by altering the degree of ionization of the cellulose surface groups (8,67). Depending on the pH change, the surface charge of cellulose can be increased or decreased, resulting in an increase or decrease in the range of the diffuse double layer. However, this question of pH is perhaps not as straightforward as presented above. In a review by Swanson (34), the pH effects alone have been shown to be negligible for the agglomeration of cellulose fibers (27,63,67). In support of pH effects, Hukki and Rinne (68) have shown changes in cellulose surface potential from -10 millivolts at pH 3 to -30 millivolts at pH 9. Hastbacka and Nordman (8) have demonstrated similar surface potential changes on pH changes, while the cellulose slurry was under the influence of Al(+3) and Th(+4) electrolyte.

POLYMER BRIDGING CONSIDERATIONS

It is possible to flocculate a system of cellulosic particles by adding polymeric retention aids, either synthetic or natural polymers (34,43,69).

The concept of polymer bridging was advanced primarily by LaMer and Smellie (70) during their work on the flocculation of phosphate slimes. The concept of polymer bridging can better be understood by referring to Fig. 2 as presented by Swanson (34). If the polymer concentration is too low, Fig. 2a, the formation of polymer bridges is unlikely since a polymer chain will likely be adsorbed entirely by a single particle. If the polymer concentration is too high, Fig. 2c, the polymer coverage is such that all attachment sites are covered and particle bridges cannot be formed. Thus, there is an optimum polymer dose, Fig. 2b, where the polymer concentration is such that the polymer can attach itself to different particles simultaneously, resulting in a flocculated particle system.

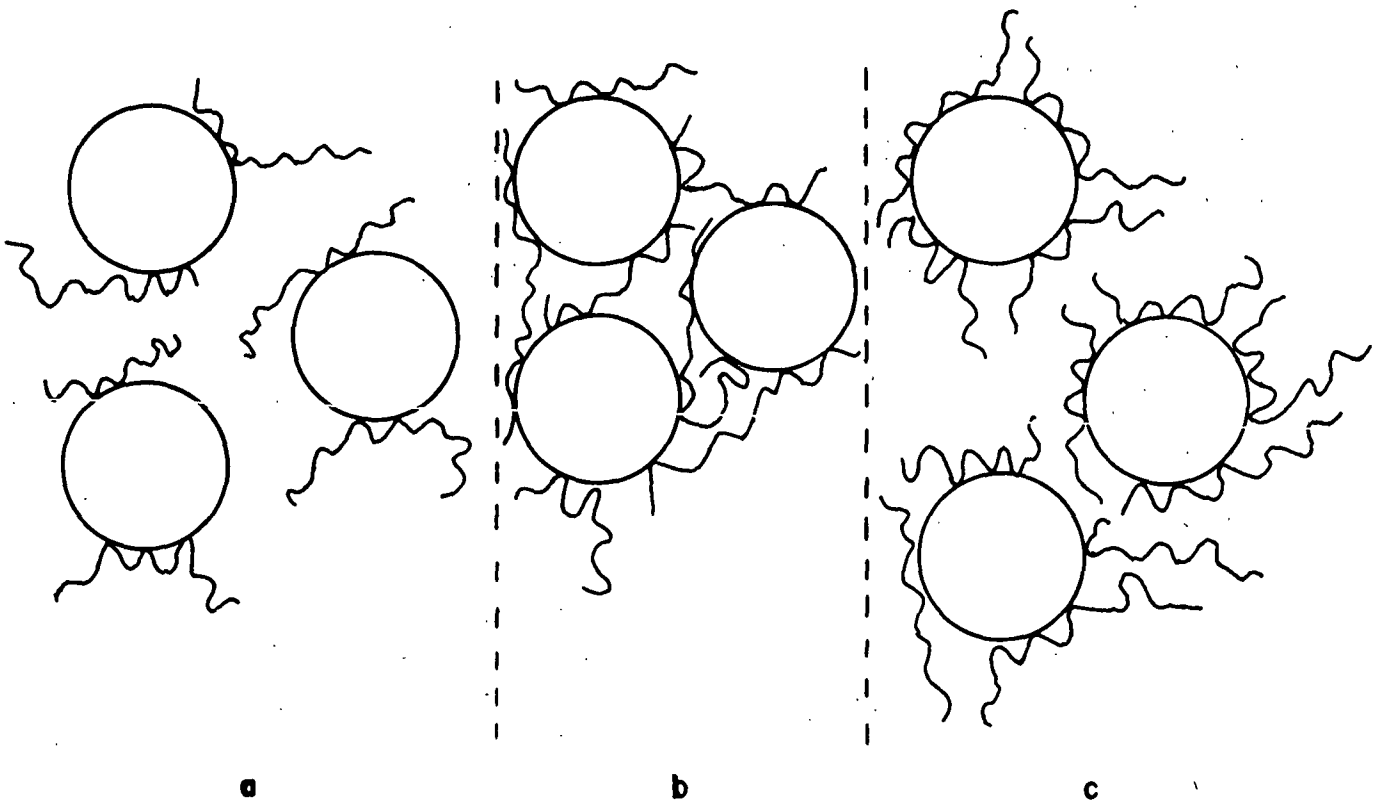


Figure 2. Representation of Polymer Bridging Mechanism

The manner and extent of polymer adsorption to the solid particle surface can also influence the degree to which a system is flocculated (71). The polymer may be electrically charged (called polyelectrolytes), interact with opposite charges of the solid surface, and form strong bonds of polymer to solid. The polymer charge may also compress the electric double layer, allowing the particles to interact with each other to a greater extent. Also, the polymer and solid particle may be of the same charge in the absence of pH or electrolyte controls, which lessens polymer adsorption and lessens the possibility of polymer bridges being formed. There may also be chemical characteristics of polymer and particle which enhance or reduce the ability of a polymer to adsorb and form bridges to the particles.

Polymer adsorption can also act as a protective influence by actually redispersing already flocculated systems (72). The protective effect is explained by noting that under certain conditions (too great a polymer concentration or prolonged agitation) the polymer can rearrange and completely cover the particles instead of forming bridges. The result is that the nonadsorbed polymer chains extending away from the solid surface establish an entropy barrier which prohibits particles from approaching near enough to form flocculated fiber networks. Even in the most idealized system, there is always a competition between the protective adsorption and the bridging adsorption, such that the flocculating power of a polymer is never 100% (28).

PRINCIPAL BACKGROUND STUDIES

There are three previous works from which the present study has primarily been formulated. These are the studies of Walkush (5), Muhonen (69), and Chiu (43). Walkush evaluated the coagulation of cellulose pulp fines and and fibers as a possible mechanism for fines retention. He employed carbon-14

radioactively tagged aspenwood fines as a means of detecting the fines retained by the fibers. His experimental variables were electrolyte type and concentration, fiber consistency, slurry agitation, and slurry temperature.

Walkush (5) concluded that coagulation via the action of simple electrolytes is an important mechanism for fines retention. It was concluded that fines retention increased as the cation concentration reached a point where the electric double layer was compressed to a maximum extent. This maximum fines retention was maintained even with the addition of excess electrolyte. The maximum retention of fines was also shown to be dependent on the fiber concentration and fiber agitation rate. In general, Walkush demonstrated that the cellulose fines and fiber systems were behaving in a similar manner to simple hydrophobic colloidal systems coagulated by electrolyte additives. Walkush concluded that retention effects were in part a result of attractive forces originating from a deep secondary energy well, that can exert its influence at low counterion concentrations if the particles are large or of irregular shape.

Muhonen (69) evaluated the nature of fiber flocculation in groundwood pulp. He evaluated the effect of polymer charge and suspension agitation on the degree of fiber flocculation. He observed that the cationic polyethylenimine and the anionic polyacrylamide which he tested enhanced cellulose fiber-to-fiber interactions, while the nonionic polyacrylamide reduced the interactions. All of his fiber interaction studies were conducted with fines present. Muhonen also demonstrated that once fiber networks were formed, they could be redispersed by the action of intense or prolonged agitation.

Muhonen's work is of special importance to the present work, in that he was able to employ a fiber optics light probe technique for the measurement

of fiber-to-fiber interactions. More will be presented on the fiber optics light probe in a later section.

Chiu's work (43) was of importance to the present study in that he was able to combine the carbon-14 technique of Walkush and the fiber optics light probe technique of Muhonen into a simultaneous measurement of fines-to-fiber and fiber-to-fiber interactions. Chiu concluded that flocculation in either a fiber-water system or in an alum-fiber-water system was a reversible process, with networks formed upon polymer addition being destroyed by prolonged agitation. Chiu (43) and Muhonen (69) noted that the degree of flocculation was dependent on the previous agitation history of the pulp slurry. The conclusions drawn from the simultaneous measurement of the fiber and fines systems were that: (1) the forces provided by alum and polymer on fines retention were the same as those on fiber flocculation, but (2) the fines-to-fiber interactions were more resistant to system agitation than were the fiber-to-fiber interactions.

FIBER OPTICS LIGHT PROBE CONSIDERATIONS

In this introductory section a discussion on the fiber optics light probe as a tool for fiber-to-fiber interactions will be presented. Studies on fiber consistency and distribution using light methods date back to 1950 with studies by Mason and coworkers (44,73). Mason evaluated fiber suspension cluster formation by detecting transmitted light through a Couette viscometer. Variations in the amount of transmitted light were used as an index of fiber cluster formation. The aggregation index, based on statistical theory, was a function of the number and size of the individual fiber aggregates.

The usefulness of the fiber optics light probe used in the current work was demonstrated during the work of Sanders (74), Nerelius, et al. (19), Persinger (35), Muhonen (69), and Chiu (43). The application of the fiber optics light probe is based on the detection of reflected light instead of transmitted light. One branch of the light guide transmits to the fiber slurry, while a second branch transmits light reflected by the fiber slurry to some detection device. Fluctuations in the reflected light intensity are related to consistency variations, i.e., the degree of fiber cluster formation.

Sanders (74) used this two branched light probe to measure time mean local consistency variations in tube flow of a suspension of bleached sulfite fir fibers. He determined the useful range of the light probe to be up to 0.80 g of fiber per 100 ml of water. He found that the consistency distribution was a strong function of both the flow rate and average consistency of the suspension. Sanders also found from his hydrodynamic studies that at sufficiently high flow rates the turbulent stresses dispersed the fibers to the point where the momentum transfer characteristics of the suspension were essentially the same as for water.

Nerelius, et al. (19), of the Swedish Forest Products Laboratory, demonstrated the ability of the fiber optics system to be applied to the measurement of fiber distributions in a papermaking system. Their probe was effective in measuring fiber distributions in stock suspensions up to 1.2% fiber in water. It was concluded from the study that the resolution of the probe was lower for flow parallel to its axis than for flow perpendicular to the probe's axis, implying that the system's resolution was dependent on the relative turbulence level and direction of particle approach to the probe.

The most recent work using the light probe is that of Persinger (35). Persinger used the technique to evaluate the fiber entanglement tendencies for fully developed turbulent tube flow using dilute synthetic fiber suspensions. The study further demonstrated the usefulness of the light probe in measuring the degree of fiber cluster formation as test conditions are varied. Persinger also concluded that local fiber cluster sizes decreased with increased local turbulence.

It has been pointed out in the preceding discussion that some of the fiber cluster size changes and distributions are affected by the suspension flow patterns about the light probe. Thus, the question can be raised, is the light probe observing changes due to a loss or gain in sensitivity rather than in an actual change of fiber cluster size? The change in sensitivity being a result of changes in speed or direction at which the fiber clusters are passing in front of the light probe. This is a valid question and probably does play a role in the light probe measurements. However, it is felt that this study has demonstrated that the light probe is capable of observing fiber-to-fiber interactions in an agitated slurry, with agitation rates at least as great as 585 revolutions per minute. The present study has been successful in monitoring colloidal flocculation and/or coagulation effects for fiber systems agitated at both 255 and 585 revolutions per minute. The fact that colloidal effects were observed even at the elevated agitation indicates that the changes in agitation were not completely overshadowing the colloidal aspects of fiber-to-fiber interactions.

REVIEW OF PROBLEM

The principal objective of this thesis program is to determine the differences and/or similarities between cellulose fiber-to-fiber and fines-to-fiber physicochemical interactions based on theoretical considerations of the diffuse electric double layer of polymer bridging, and of fiber entanglement. The major experimental variables to be studied are electrolyte type, electrolyte concentration, polymer type and polymer concentration, agitation conditions, and pH. A comparison of this type will help answer the question concerning the assumption that the fines and fibers of a papermaking system are behaving in a similar manner. These system interactions are of major importance since fiber-to-fiber interactions greatly influence sheet formation and drainage, while fines-to-fiber interactions are of great importance to the retention problems associated with the system raw materials (24,75).

The fiber-to-fiber interaction category never is isolated in a commercial papermaking slurry, but rather is always under the influence of fines materials. However, it is necessary to study a classified fiber-to-fiber system both with and without added fines in order to gain a more complete understanding of the influence of the much smaller fines materials on fiber interactions.

Typically, in the paper industry, the fiber and fines interactions are influenced by chemical and mechanical means. Chemical additives, for example simple electrolytes, are used for the control of the diffuse electric double layer of the system particles, or polymers for the control of fiber network formation via polymer bridging (76). One of the most efficient electrolytes

used in the paper industry is aluminum sulfate (papermaker's alum), where the +3 valence of aluminum and the multivalence of hydroxy-aluminum complexes are very effective in compressing and/or collapsing the double layer (13,77). This study has been formulated to use three electrolytes with cation valences of +1, +2, and +3 in order to evaluate the valence effects on cellulose particles.

Polymer retention aids can be either cationic, anionic, or nonionic in their electrokinetic properties. The charged polymers serve the dual purposes of coagulation by collapsing and/or compressing the diffuse double layer and flocculation via polymer bridging. Three polymers have been selected for this study, one of each the charge possibilities. All polymers are of the same molecular weight range and of the same backbone structure, so that system comparisons can be made without the variance of polymer molecular weight or structure.

The mechanical influences over system interactions are generally a result of the beating processes used, or the turbulence conditions of slurry pumping and sheet formation. Increased turbulence disrupts particle network formation, while beating can enhance entanglement by increasing particle surface areas. For this program, two extreme conditions of agitation will be used in order to compare the influence of agitation on particle interactions. Beating parameters will not be considered in this study because of the already large number of variables to be evaluated.

As discussed in the introductory section, pH can have an influence on the extent of particle and additive interactions. Thus, pH will be varied in such a way as to evaluate acidic, basic, and neutral slurry conditions normally encountered in paper furnishes.

The experimental techniques are now available to monitor the cellulose fines and fiber systems. By using the two branched fiber optics light probes in conjunction with the radioactively tagged carbon-14 tracer technique, it will be possible to follow fiber-to-fiber and fines-to-fiber systems simultaneously. By classifying the cellulose test fibers, it may be possible to obtain test fiber systems both with and without fines.

Before proceeding to the experimental details of the thesis program, a concise summary of the objectives and goals of the program is listed below.

1. To determine the similarities and/or differences in colloidal coagulation and/or flocculation parameters of a cellulose fiber-to-fiber system with fines, a cellulose fiber-to-fiber system without fines, and a cellulose fines-to-fiber system, as related to electric double layer theory, polymer bridging theory, and fiber entanglement theory. This objective is concerned with demonstrating how cellulose fiber and fines systems behave in their colloidal aggregation properties while in a water environment. To demonstrate, it is indeed possible to disperse cellulose fibers while maintaining fines retention as a result of the large difference in the surface area of the fines and fibers on a weight basis.

2. To determine the effects of agitation on cellulose fiber and fines systems, while demonstrating how these agitation conditions influence colloidal coagulation and/or flocculation tendencies.

3. To extend present knowledge as to the usefulness of the fiber optics light probe technique as a means of measuring the extent of fiber cluster formation in a pulp slurry. The light probe technique is a fairly recent tool to be used by the paper industry, with some successes as well as some problems encountered during its use. It is felt that a demonstration of the use of the light probe method in the present study will supply evidence either in support of or against the use of the light probe by the paper industry.

EXPERIMENTAL

MATERIALS

Test materials used in this study and discussed in this section include the radioactive fines, the classified fibers, system water, test electrolytes, and test polymers.

RADIOACTIVE BLEACHED KRAFT ASPEN FINES

The radioactively tagged carbon-14 fines used in this study were the fines remaining from the Walkush study (5). The fines were obtained by Walkush from trembling aspen seedlings, which had been grown in an atmosphere of carbon-14 dioxide. A complete schedule and description of the treatment procedures used by Walkush and results of the seedling growth is presented in Appendix I. After the seedlings were harvested, the branch stems were debarked and cut into 0.75-inch lengths. The wood was prepared for pulping by extraction with alcohol: benzene, alcohol, and water according to TAPPI Standard T 12 m-57.

Walkush pulped the wood kraft process at typical pulping conditions in small, 500-ml bomb digesters. A detailed description of the pulping conditions is presented in Appendix II. The pulp was washed and bleached with a 10% acidified sodium chlorite solution at 1% consistency for 14 days at room temperature. The bleached pulp was washed thoroughly with distilled water, thickened, and air dried.

Walkush prepared the fines materials from the bleached carbon-14 pulp via the following procedure. A Virtus "45" homogenizer was used to reduce the radioactively tagged pulp into fibril-like fines. Particle size reduction was accomplished via the shearing and cutting action of a razor-sharp 1.0-inch

blade rotating at 45,000 rpm in a 125-ml convoluted sample container. The homogenizer was designed for rupturing concentrated suspensions of microorganisms (78). After homogenization, a series of centrifugations was used to separate the fines into well-defined fractions according to particle size. Walkush found that the fines could be preserved by freezing without having to add formaldehyde or any other biostatic agent which might have interfered with colloidal properties. Thus, the fines were frozen in polyethylene bottles in convenient 200-ml volumes. The approximate frozen fines concentration was 0.0024 g/ml.

Walkush used a Coulter Counter, Model B, for the determination of fines particle size (79). He reported weight average and number average equivalent spherical diameters of 1.11 and 1.07 μm, respectively, for the fines particles. The radioactively tagged fines were chemically characterized by The Institute of Paper Chemistry's analytical group for monosaccharide content and total carboxyl content; Walkush determined the specific activity of the fines. Specific activity is defined as the radioactive counts per minute for one gram of oven-dried fines sample. The results of the chemical analysis plus the specific activity determinations of the fines are given in Table I for the fines of Walkush and the current fines. Notice that there are some differences in the absolute numbers of the Walkush fines and the current fines. It was felt that the differences were not great enough to significantly alter current system comparisons.

As mentioned previously, Walkush separated his carbon-14 fines into fractions according to particle size, freezing four fractions: (1) "very fines" of particle size less than 0.75 μm, (2) "fines" of particle size 0.75 to 4.02 μm, (3) "fines sediment" containing particles between 4.62 and 9.25

μm, and (4) "grinding sediment" containing particles larger than 9.25 μm. He used the fines fraction, 0.75 to 4.62 μm, for his retention study, but for the present program there was not an adequate supply of this fraction. Therefore, the three fractions from 9.25 μm down were combined to insure an adequate supply of carbon-14 fines. Walkush's fines were thawed and combined in a 4-liter glass-stoppered bottle. Formaldehyde was added to the fines slurry for a 0.1% by weight of fines concentration.

TABLE I

CHARACTERIZATION OF RADIOACTIVE FINES

Monosaccharides, % by weight	Walkush	Current
Glucose	77.6	74.0
Xylose	16.5	16.4
Mannose	0.4	0.2
Arabinose	0.3	0.1
Galactose	0.5	0.1
Total carboxyl content, mM/100 g	5.9	--
Specific activity, cpm/g	4.17×10^7	3.78×10^7

Two different specific activities were determined for the fines combination used in this study. One was for the entire energy spectrum of carbon-14 and is the same type determined by Walkush. The second activity was for a narrow carbon-14 spectrum, which excluded the low energy carbon-14 responses. The carbon-14 narrow window was selected for this study, since it was more sensitive at the low radioactive counts encountered (80).

The specific activities were 1.858×10^7 cpm/g for the narrow window and 3.781×10^7 cpm/g for the wide window. The last value compares to the

value of 4.17×10^7 cpm/g for the Walkush fines (Table I). This small discrepancy is a result of weighing errors for the very small samples required for the determination (80). No additional carboxyl determinations were made, since the fines were in relatively short supply.

BLEACHED KRAFT ASPEN FIBER

The major thrust of the present study was to compare interactions of fines and fiber systems. Thus, for these comparisons to be more meaningful, it was important that the fines and fibers be as nearly the same chemically as possible. Already having the bleached kraft aspen fines of Walkush, it was decided to carry the fibers through as nearly the same pulping and bleaching conditions as Walkush had used for the fines. An aspen log was debarked, chipped, and pulped via the kraft process, followed by an acidified sodium chlorite bleaching. A complete description of the pulping and bleaching procedures used by the current author is presented in Appendix III. Walkush used an extended bleaching period at room temperature, but Peckham (81) noted that the elevated temperature bleaching for a shorter time used in this study would produce pulp of approximately the same characteristics as did Walkush's procedure.

The resulting pulp was classified to remove the system's fines by two passes over The Institute of Paper Chemistry's web former equipped with a 70 × 54 semitwill bronze wire. The resulting fibers were stored at approximately 20% solids in polyethylene bags with a formaldehyde preservative. The pulping and bleaching procedures were conducted for two aspen logs at two different times during the course of the study.

Samples of test fibers were submitted to The Institute of Paper Chemistry's analytical group, engineering group, and physical chemistry group to determine monosaccharide and total carboxyl, hydrodynamic specific surface area and volume, and average fiber length and width, respectively. The results of these analyses are presented in Table II, with a more detailed description of the analyses located in Appendix IV.

TABLE II

CHARACTERIZATION OF SYSTEM TEST FIBERS

Monosaccharide, % by weight[b]	Sample 1[a]	Sample 2[a]	Sample 3[a]
Glucose	81.0	81.7	77.0
Xylose	15.7	15.1	17.1
Mannose	0.9	0.7	0.9
Galactose	0.6	0.3	0.7
Arabinose	0.2	0.1	0.3
Total carboxyl, mM/100 g[b]	6.04	5.60	6.20
Specific fiber surface area, cm^2/g[b]	10,500	9,900	11,600
Specific fiber volume, cm^3/g[b]	2.92±4.0%	2.70±4.0%	2.76±4.0%
Arithmetic average fiber length, mm	0.83	--	0.87
Weighted average fiber length, mm	0.95	--	0.94
Arithmetic average fiber width, μm	16.9	--	15.9
Weighted average fiber width, μm (including vessel elements)	18.4	--	20.4

[a] Sample 1 is fiber batch I, 3 months after pulping.
Sample 2 is fiber batch I, 9 months after pulping.
Sample 3 is fiber batch II, immediately after pulping.

[b] All values are single point determinations. Fiber surface area and volume were determined by a filtration resistance technique.

The monosaccharides, total carboxyl contents, specific volumes, fiber widths, or fiber lengths, did not vary significantly either with time or with different fiber batches. However, there did appear to be a decrease in the surface area of fiber batch I upon storage. Fiber batch II was checked for surface area changes after 3 months of storage, resulting in a surface area of 11,600 cm^2/g. This value indicates that the surface area probably was not changing as a result of prolonged storage.

It is also important to note that the monosaccharide contents of current test fines (Table I) and of the present test fiber (Table II) were very nearly the same, as was hoped by selecting the same wood species with similar pulping and bleaching conditions.

WATER

High quality water was required for this study since ionic species, organic materials, or other impurities in the water might have had an influence on the surface properties of the cellulose materials. Therefore, the water used was both deionized and distilled. Test water was used only if its specific conductivity was less then 1.2×10^{-6} mhos/cm. Appleton city water was deionized and then distilled in the Barnstead still of the analytical group at The Institute of Paper Chemistry. The water was collected and stored in two 10-liter glass bottles. Conductivity determinations were taken periodically on the stored water to establish its usability.

ELECTROLYTES

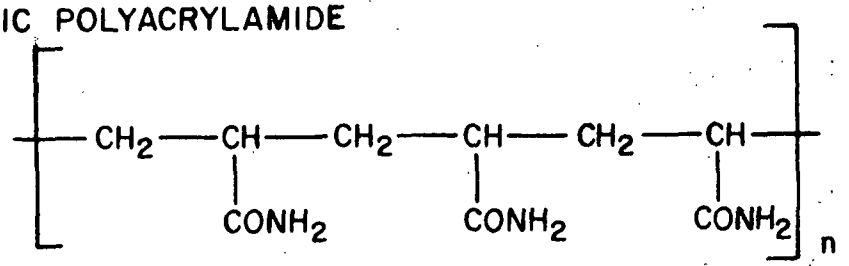
There was a twofold purpose behind the selection of the system test electrolytes. First, it was desired to have a series of electrolytes with a common anion, while having cations with different valence. Thus, it was

possible to compare the effects of the differently charged electrolyte cations on the compression and/or collapsing of the electric double layer. Second, Walkush had evaluated the effects of La(+3), Ca(+2), and Na(+1) on fines retention, so that some of Walkush's data could be used in comparing fines-to-fiber and fiber-to-fiber interactions if similar cations were used. Thus, $LaCl_3$, $CaCl_2$, and NaCl were selected as the test electrolytes. The $LaCl_3$ was a Fisher Scientific Company certified grade, while the $CaCl_2$ and NaCl were Baker reagent grades. The NaCl was a crystalline solid, the $CaCl_2$ was an anhydrous solid, and the $LaCl_3$ was hydrated with six molecules of water. The electrolytes were prepared in one-liter stock solution quantities and stored in one-liter glass-stoppered reagent bottles until needed. The stock solution concentrations were confirmed by analytical department analysis.

POLYMERS

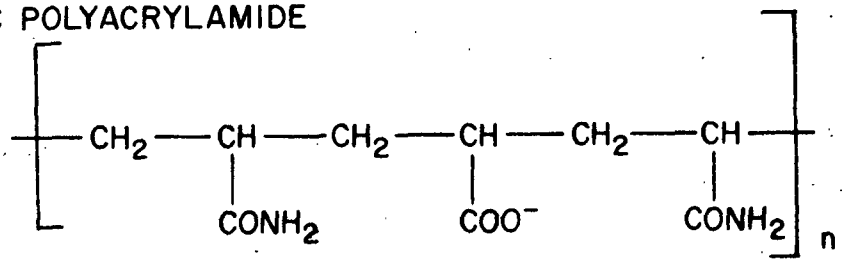
As was stated previously, it was a goal of this study to compare the charge effects of polyelectrolytes on the flocculation of cellulosic materials without the effect of polymer chain structure or molecular weight. American Cyanamid Company supplied this study with a series of polymers, all of which had approximately the same weight average molecular weight of 2-4 million, with the same backbone chain chemical composition. The polymers were all polyacrylamides differing only in their ionic charge. Magnifloc 560C was a cationic copolymer containing 4-6% of a tertiary amine, while Accurac 24+ was an anionic copolymer containing 2-4 mole% of acrylic acid. Representative structures of the nonionic polymer, Superfloc 16, along with the Accurac 24+ and Magnifloc 560C are described in Fig. 3. All three polymer samples were commercial products and were not well-characterized research grades.

NONIONIC POLYACRYLAMIDE



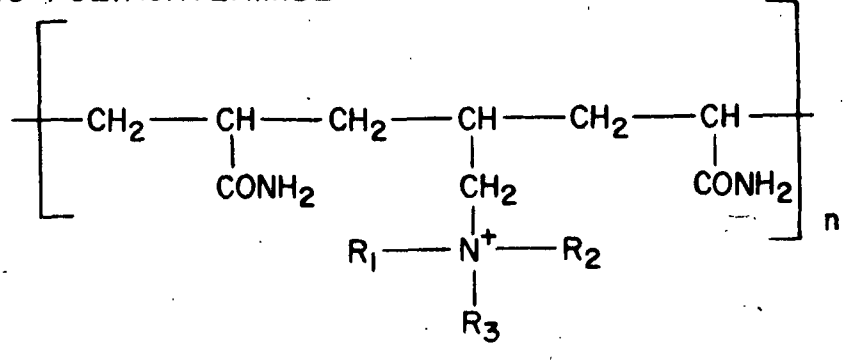
SUPERFLOC 16

ANIONIC POLYACRYLAMIDE



ACCURAC 24+

CATIONIC POLYACRYLAMIDE



MAGNIFLOC 560C

Figure 3. Representative Polyacrylamide Polymer Structures

The solid polymers were dissolved in distilled water by adding to water agitated severely enough to create a large vortex in the liquid. The polymer was completely in solution after three hours agitation, but the solution was gently agitated for 12 additional hours before use. The polymer solutions were formulated to 0.1% polymer in water by weight, with the stock solutions used in all cases within a 24-hour period after the initial solution process. It was necessary to use these stock solutions as soon as possible since polymer solutions will undergo degradation and loss of flocculating power upon storage. For example, Shyluk and Stow (82) have demonstrated the loss of flocculation activity for polyacrylamide upon aging in water. The loss of flocculation activity was attributed to a weakening of inter-particle bridging. It was realized that the current system would undergo some degradation within the 24-hour period of polymer use. The only way to get by this problem would be to make fresh polymer for each test evaluation. However, the three hours required to get the polymer in solution coupled with the large number of test systems prohibited fresh polymer formulation for each test. As long as the data were reproducible using the polymer within a 24-hour period, the 24-hour period was considered an adequate turnover time.

APPARATUS

There were two primary systems for which experimental apparatus was required. These were the fiber-to-fiber and fines-to-fiber interacting systems.

FIBER-TO-FIBER

The experimental apparatus used to follow the fiber-to-fiber interactions can be thought of as two units in combination, where one unit was the mechanical part of the apparatus and the second unit was the detection part of the apparatus.

The mechanical part consisted of a containing vessel for the fiber slurry, a light source, a two-branched fiber optics light probe, a cellulose fiber slurry agitator, and an AutoAnalyzer pump. The fiber slurry was placed in the containing vessel and agitated by a three-bladed impeller. Light from the light source was passed through one branch of the light probe, reflected by the fibers in the tank, and passed back through the second branch of the light probe. Flushing water was required to prevent the fibers from sticking or stapling to the end of the light probe. Thus, the AutoAnalyzer pump served the purpose of pumping water from the tank to the tip of the light probe while maintaining constant fiber consistency. The tip of the light probe extended approximately 1/8 inch from the flushing jacket. The 1/8 inch resulted from the amount of the probe coming through the containing vessel which was not surrounded by the water flushing jacket. If desired, the length of probe extending into the slurry could be varied by changing the length of the water jacket. The flushing line was also used as a sampling line for fines systems.

The flushing line extended into the fiber slurry, so that fibers had a tendency to staple to it also. This problem was solved by Chiu (43) with the addition of a mechanical vibrator attached to the flushing line through a series of clamps just before the tube entered the fiber slurry. By

shaking the tube at a high frequency and low amplitude, the fibers were prevented from sticking to the sides of the flushing tube.

The containing vessel was a clear Lucite tank wrapped in black electricians tape to exclude external light. The tank was 5.0 inches in diameter and 8.0-inches high. The slurry agitator was a 1/5-horsepower Bodine Motor, Model NSH-34, and was used to drive a three-bladed impeller with a blade pitch of 45°, blade length of 0.5 inch, and hub diameter of 0.5 inch. The impeller was located on a shaft 7.25 inches from the drive motor. These dimensions resulted in the impeller resting 0.75 inch from the tip of the fiber optics light probe. A complete diagram of the impeller positioning will be presented in Appendix XI where impeller angles are discussed. The revolutions per minute (rpm) of the agitator were controlled by a solid-state Minarak variable speed controller, Model SH-53. The light source used to supply light for one branch of the light probe was equipped with a variable focus, and with the following electrical supplying system. Line voltage was fed to a Sorensen Model 150-S dc power supply. Next, the signal was passed through a Chicago Stancor RT-204 stepdown transformer followed by a 0.5-ohm resistor in series and a 31,500 microfarad capacitor in parallel, before entering the Model 1960 quartz-iodine lamp.

A two-branched fiber optics light probe was employed, with the glass fibers arranged in a concentric design. The probe used in this study was the same type as was used by Sanders (74). The outer circle of glass fibers was used to transmit light from the light source to the fiber slurry. The inner bundle of glass fibers was used to transmit the light reflected by the fibers to the detection circuitry. The probe is represented in Fig. 4, with the overall length of the probe at 2.0 feet and the radius of the probe

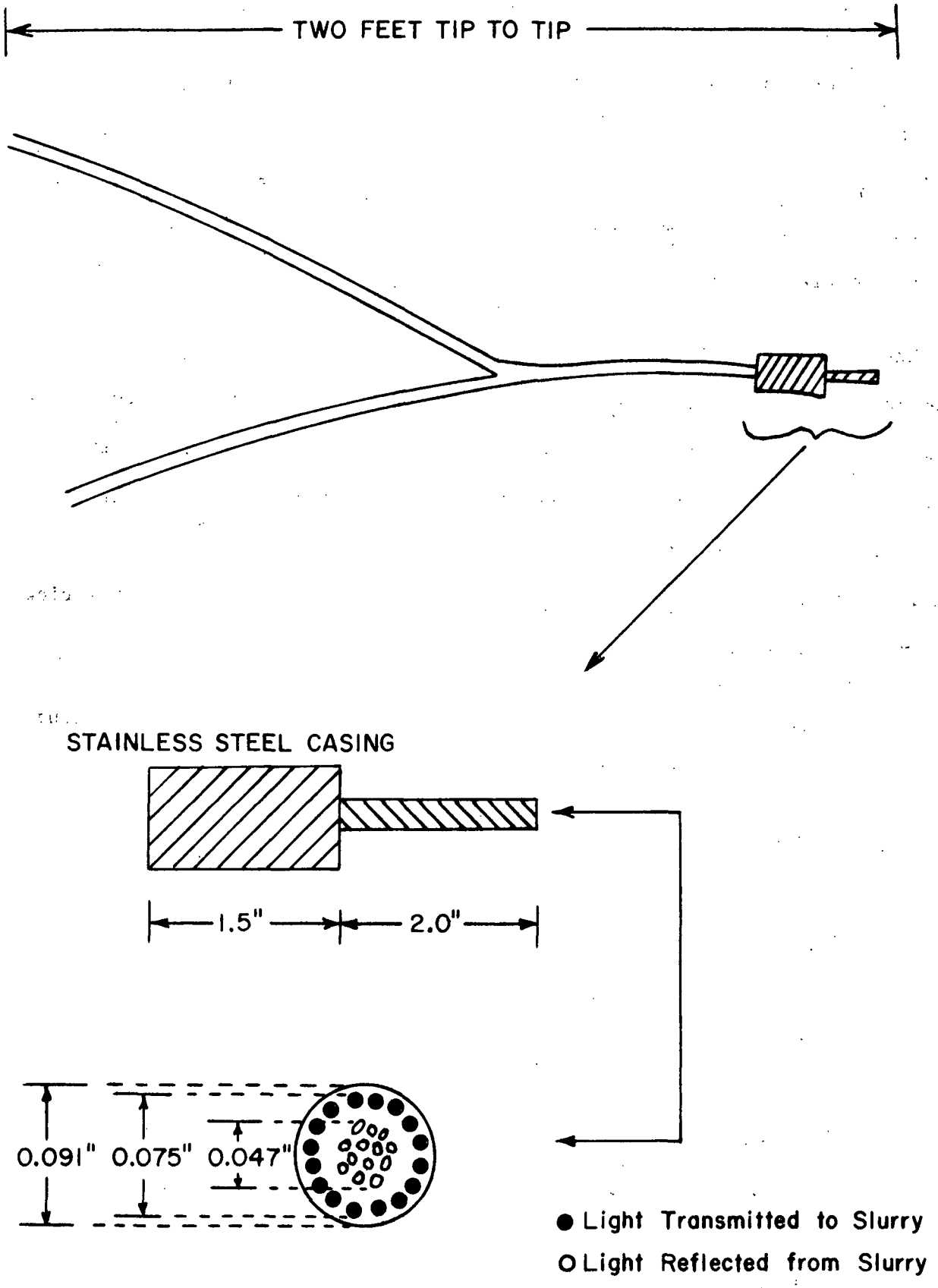


Figure 4. Two-Branched Fiber Optics Light Probe

tip at 0.091 inch. The stainless steel casing at the end of the probe was the point where the glass fibers of the two individual branches were brought to a common end. The 2.0 inches of the smaller section of the stainless steel casing was inserted into the Lucite vessel all the way up to the large section of the casing. The probe was built and supplied by the American Optical Corporation, Fiber Optics Division.

The AutoAnalyzer pumping system was fitted with 1/8-horsepower variable speed dc Bodine motor, Model NSH-54RL, controlled by a Minarak speed controller Model SH-53. Three tube sizes were used to recycle the water. The first tube coming from the tank was standard AutoAnalyzer tubing of 0.045-inch inside diameter. The center tube passing through the pump was standard AutoAnalyzer tubing of 0.100-inch inside diameter. The flushing jacket tubing was teflon tubing of 0.140-inch inside diameter.

The equipment described to this point is shown in Fig. 5, with a listing of the apparatus by number given below:

1. ac Regulator
2. dc Power supply for light source
3. Light source
4. Fiber optics light probe
5. Power supply for agitator motor
6. Agitator motor
7. Lucite containing vessel
8. Power supply for AutoAnalyzer pump
9. AutoAnalyzer pump
10. Mechanical vibrator

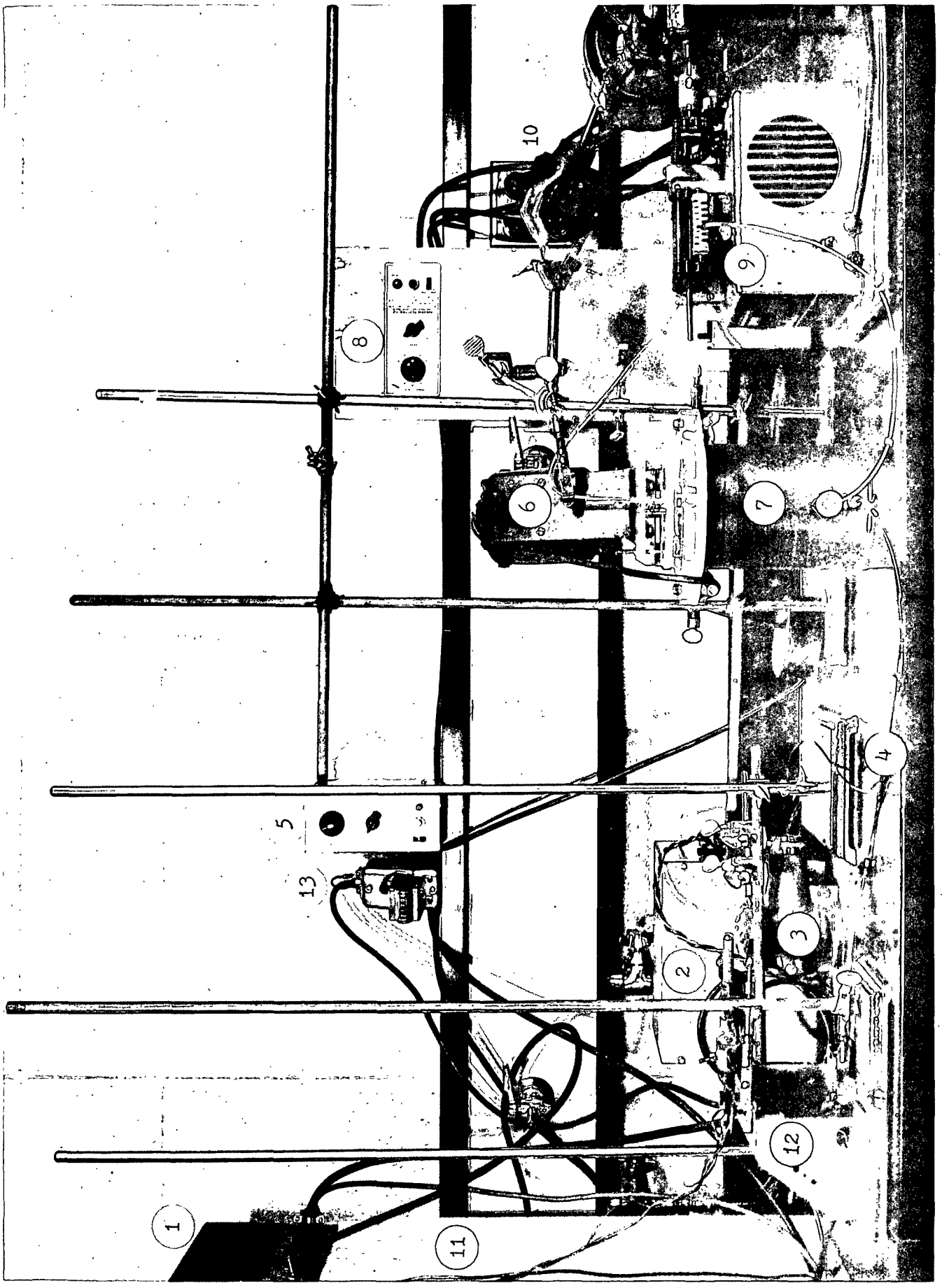


Figure 5. Experimental Apparatus Mechanical System

The detection equipment picks up the reflected light for the second branch of the light probe and turns the light into electrical signals, which are measured and converted into basic data. This detection equipment consists of a photoresistor to change the light intensity into electrical signals, a wheatstone bridge circuit with null indicator meter for indicating the magnitude of the electrical signal, and a camera system to record the deflections of the null meter.

The photoresistor and null indicator meter were parts of the wheatstone bridge circuit shown in Fig. 6. The photoresistor was placed in front of the reflecting end of the light probe, and depending on the amount of light received by the photoresistor, needle deflections were registered on the null meter. There were two variable resistors in the wheatstone bridge circuit for the purpose of balancing the bridge circuit as indicated by the null meter; one resistor (200,000 ohms) was a coarse adjustment and the other resistor (5000 ohms) was a fine adjustment. The null meter was a Doelcam magnetic null detector, Model 2HG-1, while the photoresistor was a Clairex CL-705L photocell.

A Cine-Kodak 16-mm movie camera was used to photograph the null indicator meter at a frequency of one every two seconds. The camera was an old Kodak model, which did not have a workable shutter system; thus it was necessary to place the entire camera system in a light tight box, exposing the film with a Rollie E-17 electronic photoflash. A motor drive was designed, which tripped the flash unit every two seconds, while tripping two numerical counters. One counter was within the view of the camera lens, providing a means of counting individual pictures after development. The second counter was external to the light tight box enabling the operator to

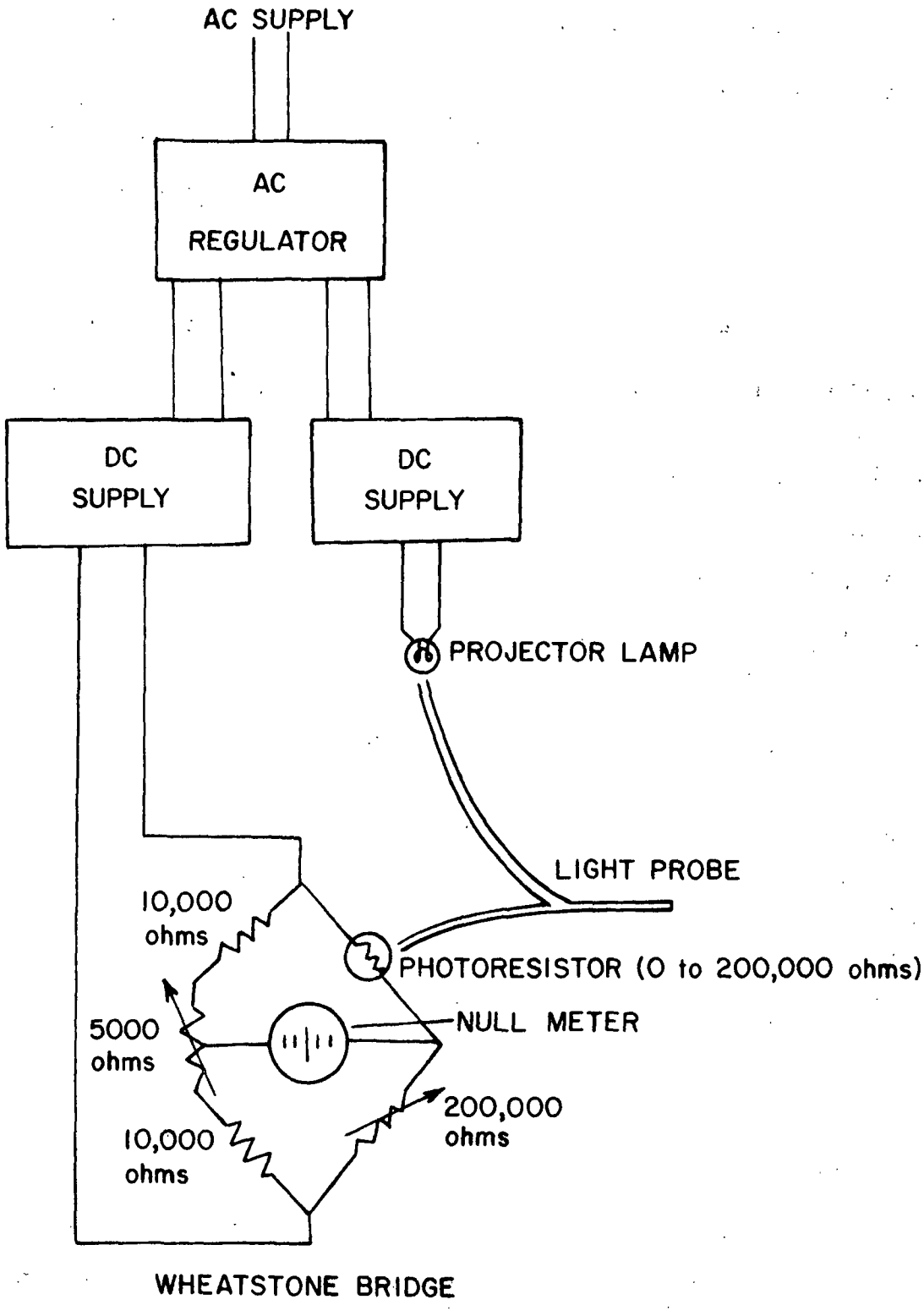


Figure 6. Experimental Apparatus Wheatstone Bridge Circuitry

determine the number of pictures taken. The exposed film was developed for 3 minutes and 20 seconds in Kodak developer and for 5 minutes in a Kodak sodium thiosulfate solution. The null meter values were read from the images on the developed film with a Kodak microfilm reader. For all evaluations, the movie film was advanced by a 1/30-horsepower Bodine motor, Model CEG-2, at approximately 1.25 frames per second.

The detection equipment described to this point is represented in Fig. 7, with an identification list as follows:

1. Null indicator meter
2. Internal frame counter
3. Light tight box
4. 15-Volt dc power supply for wheatstone bridge circuit
5. ac Regulator
6. Camera motor drive, switches for photoflash and counters
7. 16-mm Movie camera
8. Electronic photoflash

Detection equipment shown in Fig. 5 is listed below:

11. Light tight box
12. Photoresistor and variable resistors
13. External frame counter

FINES-TO-FIBER

The fines-to-fiber apparatus was essentially the same as for the fiber-to-fiber equipment, except that the fiber optics light probe was not in operation. Samples of the recirculating supernatant were analyzed for carbon-14 by a liquid scintillation counter.

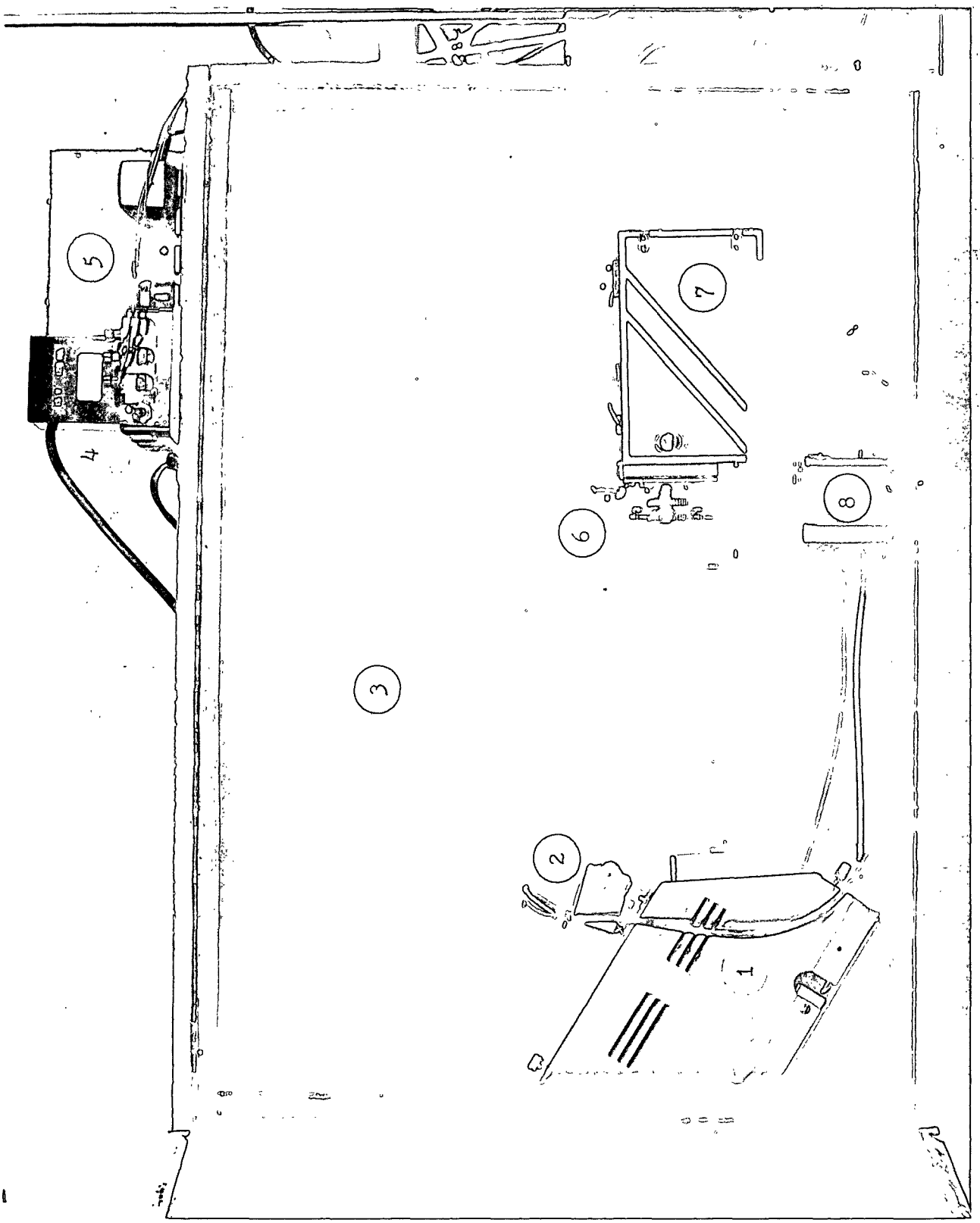


Figure 7. Experimental Apparatus Detection System

The fines and fiber slurry was placed in the same Lucite vessel as described previously and agitated with the same impeller set up. The Lucite vessel was equipped with a sample port to which the reflushing tube was attached. This port was covered with a 35-mesh stainless steel wire screen, having a pore size of 420 μm and an open area of 33.8%. The classified pulp fibers did not pass through this screen in any significant amount, while the fines materials did pass through the screen with little difficulty. The AutoAnalyzer pumping system and the mechanical vibrating system were used in the same way as described previously for the fiber-to-fiber interactions.

The activities of the radioactive fines samples obtained through the sample port were determined by liquid scintillation counting on a Beckman Model LS-100 liquid scintillation counter (83). The instrument indirectly measured radioactivity by measuring the ultraviolet light emitted by a phosphor,2,5-diphenyloxazole, upon bombardment by the emission particle. The counting samples contained approximately 2.0 ml of fines supernatant in 15 ml of counting cocktail. The counting cocktail was composed of 10 g of 2,5-diphenyloxazole and 200 g of naphthalene diluted to 2 liters of 1,4-dioxane. The results obtained from the scintillation counter were the basic experimental data.

PROCEDURES

The procedures used in this study will be covered in three parts: (A) the fiber-to-fiber studies, (B) the fines-to-fiber studies, and (C) supportive studies. The simultaneous measurement of a fiber-to-fiber system and a fines-to-fiber system will be treated as if the fines were additives to the

fiber-to-fiber system. Each individual system will be presented as if describing a typical evaluation.

FIBER-TO-FIBER INTERACTIONS

The classified fibers were transferred to a small polyethylene bag from the large storage bag. This smaller bag of fiber was stored in the refrigerator with a formaldehyde preservative for at least 12 hours before use. Prior to the test evaluation, a predetermined quantity of fiber was added to a predetermined amount of distilled water, such that the fiber consistency was maintained at 0.5% for the evaluation. The distilled water was always filtered through a Millipore filter of 0.45-μm pore size into a 2000-ml vacuum flask. The Millipore filter served to remove impurities present in the water. Water pH was adjusted to 5, 7, or 9 within ±0.2-pH unit by adding either HCl or NaOH prior to the addition of any cellulose material. It was determined that adding the cellulose did not alter system pH. The pH was determined with a Corning Model 12 research pH meter. The fiber slurry was next deaerated 15 minutes under laboratory vacuum conditions. This step also served as the dispersion step, since the slurry was being agitated with a 2.0-inch teflon-coated magnetic stirring bar rotating at 182 ± 5.5% rpm. The speed of the stirring bar was determined with an electronic Strabotac supplied by the Institute's Container Division.

During the 15-minute deaeration and dispersion time, the fiber optics light probe was calibrated, bringing the light intensity to the same level for each test system. The light source was operated for 30 minutes before calibration. The tip of the fiber optics light probe was inserted into a water-filled light-tight polyethylene container to the same depth for each calibration. The imbalance of the wheatstone bridge was measured on a

microammeter making certain that the fine variable resistor of the bridge circuit was always turned fully clockwise. The coarse adjustment variable resistor was secured and remained in the same location for the entire study. The null indicator meter was always switched off during the calibration. The focal adjustments on the light source were used to bring the microammeter to the same reading for each run. Adjustments were made infrequently, as the light intensity did not vary greatly.

After the 15-minute deaeration and dispersion period, the fiber slurry was transferred from the vacuum flask to the Lucite test vessel. Two agitation conditions were used in the present study, a rather severe high agitation condition of 585 rpm and a mild low agitation condition of 255 rpm. The fiber slurry was always preagitated before a test evaluation for 5 minutes at 585 rpm followed by 5 minutes of agitation at either 585 or 255 rpm, depending on which test rpm was to be used for the evaluation. For all systems, the AutoAnalyzer pump was operated at a flow rate of 15.0 ml/min and the vibrator was switched on during the last minutes of the preagitation period. This 10-minute preagitation period was necessary to insure that all fiber systems experienced the same agitation history. Chiu (43) and Muhonen (69) have shown that the degree of fiber flocculation was dependent on the previous shear history of the fiber sample.

At the end of the 10-minute preagitation period, 100 pictures were taken of the null meter at two-second intervals. The slurry fiber was then discarded, the system washed, and readied for the next run. At least two duplicate runs were made for each test condition, and in many cases more than two runs. Refer to the correct Appendix in order to determine the number of test evaluations.

There were three additive types used in the fiber-to-fiber work: electrolytes, polymers, and fines. For the test evaluations using these additives, the fiber slurry was agitated for 5 minutes at 585 rpm before adding the chemicals and/or fines. The 10-minute preagitation period was then carried out just as described earlier, followed by the collection of 100 data points. In all cases, the additives were added to the slurry tank from either graduated or volumetric pipets. When additives were involved, the final fiber concentration at the time of data collection was maintained at 0.5% fiber by weight for all experimental systems.

FINES-TO-FIBER INTERACTIONS

The combined fines of Walkush had to be redispersed before they could be used in this study. In all evaluations where fines were required, the fines were dispersed with the Virtis "45" homogenizer. Ninety milliliters of the test fines at 0.0024 g/ml were placed in a 125-ml convoluted Virtis flask, the flask being packed in ice to hold down temperature build-up. The fines were dispersed by the action of the Virtis "45" homogenizer blades rotating at 37,000 rpm for 10 minutes. Next, the fines were deaerated under vacuum for 15 minutes with gentle agitation. After the deaeration, the fines were ready for addition to the test vessel. Fines were added to the extent of 1.0% by weight of fiber present, except for one study where a 10% fines addition was used. Preagitation and test conditions were as described earlier.

Test samples for the scintillation counter were collected at two different times depending on the type of test being conducted. For systems where fiber-to-fiber and fines-to-fiber interactions were being followed simultaneously, the fines samples were collected through the sample port

only after the collection of the 100 data points for the fiber-to-fiber test. For systems where the fiber-to-fiber interactions were not being followed, then the fines samples were collected at the end of the preagitation period.

For each test situation, three 2.0-ml samples of fines supernatant were collected via a gravity feed through the sample port. The supernatant was back forced through the sample port by air pressure just prior to sample collection for the purpose of completely freeing any materials trapped in the openings of the 35-mesh screen. The collected samples were counted on the liquid scintillation counter for 20 minutes, generally to a standard deviation of 1.5%. The three sample count rates were averaged and used in the determination of system results. A typical error in this averaged value was ±3.9%, which will be elaborated on in a later section.

SUPPORTIVE STUDIES

There were five major supportive studies conducted throughout this work, which required slightly different procedures than already described. These studies included: (1) a time of agitation evaluation on test fibers and fines, (2) an impeller blade number evaluation on fiber cluster formation, (3) a polymer adsorption evaluation on test fiber, (4) an accelerated aging evaluation on the test fibers, and (5) a sodium hydroxide extraction evaluation on test fiber.

(1) A study was conducted to determine the effect of an extended period of agitation on the fiber-to-fiber and fines-to-fiber interactions. In this evaluation one fiber and fines slurry, after preagitation, was agitated at 585 rpm for 5 minutes, then at 255 rpm for 5 minutes, followed by data collection

for first the light intensity measurements and lastly for the carbon-14 measurements. This agitation cycle was repeated for a total time of 30 minutes at 585 rpm.

In a separate time of agitation study, the degree of fiber cluster formation was monitored for a 23-hour period at both 255 and 585 rpm. For this study, a fiber slurry was agitated at 255 and 585 rpm over a 23-hour period, with data collection at various times during the 23-hour period.

(2) An evaluation was conducted for the purpose of determining whether or not the changes in fiber cluster formation observed between 585 and 255 rpm were truly a result of fiber cluster formation or destruction. It was pointed out by Meyer (84) that observed differences between 585 and 255 rpm may have been due to the changing cutting action of the impeller blades instead of as a result of changing hydrodynamic agitation conditions.

A specially designed impeller was constructed with six blades of the same pitch and size as the standard three-bladed impeller normally used. The hubs of the two impellers were the same diameter, and the two props could be positioned at exactly the same position in the tank with respect to the light probe's position. The six-bladed impeller was used to evaluate fiber-to-fiber systems with the cationic polymer at pH 7 for both the low and high agitation conditions. Agitation and test conditions were the same as described previously.

(3) A polymer adsorption study was conducted in order to determine the amount of polymer adsorbed on the cellulose fibers. The polymer-fiber slurries were formulated and agitated exactly as described in the fiber-to-fiber section. Cationic systems were tested at pH 5.0, anionic at pH 9.0, and nonionic at pH 9.0. At the end of the preagitation period, the supernatant was filtered off through a coarse glass filter. The filter pore size was 40-60 μm, so that the unattached fines materials could pass through the filter openings. The fiber was washed with 1.0 liter of distilled water to remove as much of the unattached materials as possible. The fibers were then submitted to The Institute of Paper Chemistry's analytical group for a micro-Kjeldahl nitrogen analysis. Appropriate control samples were also analyzed, so that a percentage polymer on fiber determination could be made.

(4) An accelerated aging study was conducted for the purpose of determining the effects of fiber aging during storage on fiber cluster formation. Two aging conditions were employed. In one the fiber was aged for one week at room temperature in a sealed container, and in the second the fiber was aged for 13 hours at 105°C in a sealed container. Measurements on the aged fiber systems were conducted with no additives and with $LaCl_3$. Unaged control samples were monitored throughout the study. Test procedures outlined for the fiber-to-fiber interactions were used in these fiber aging studies.

(5) A sodium hydroxide extraction study was conducted for the purpose of determining whether or not the extractables remaining after pulping and bleaching would affect fiber cluster formation tendencies. Two NaOH concentrations, 0.25 and 0.75%, were used in the evaluation, with the fiber being heated in the NaOH solution for one hour at 105°C as described by Casey (85). Fiber-to-fiber interaction evaluations for the extracted fibers were conducted as described previously.

REDUCTION OF DATA

All data collected in this study werein two forms only, one being from the null indicator meter values (film recorded) for the fiber-to-fiber interactions, and the second being from the liquid scintillation counting for the fines-to-fiber interactions.

FIBER-TO-FIBER

In this study, the degree of fiber cluster formation is defined as the standard deviation of the intensity of the reflected light as seen by the fiber optics light probe. It was assumed that the null indicator meter readings were directly proportional to the changes of light intensity seen by the photoresistor in front of the light probe. Deflections of the null meter resulted from photoresistor voltage changes across the wheatstone bridge circuit. The works of Muhonen (69) and Chiu (43) support the assumption that the indicator readings were indeed a measure of the fiber interactions in the Lucite vessel. Mason and coworkers (44) subjected a suspension of cellulose fibers to a reproducible condition of shear motion and electronically analyzed the fluctuations in optical transmission

coefficient. Mason, et al., presented a flocculation index, which was both a function of aggregate number and size. In Mason's treatment, the standard deviation of light fluctuations (s) was shown to be a measure of fiber aggregation.

For the current study, when the pulp was well dispersed, the slurry would appear fairly uniform to the light probe, resulting in only a small variation in back-scattered light intensity and thus a small standard deviation would result (Fig. 8). However, if there was a large variation of fiber cluster size in the slurry, then the light probe would see many different sized particles, resulting in a wide variation in back-scattered light intensity. A large standard deviation would result (Fig. 8).

The spread of the observation frequency distribution curve provided a measurement of the degree of fiber cluster formation. This spread was expressed as a standard deviation,

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}} \qquad (1)$$

where x_i = meter reading

$\bar{x}$ = average of meter readings

n = number of observations

In all experimental data figures presented in this paper, the standard deviation (s) is plotted on the y axis versus additive concentration. A computer program was written to handle the 100 data points read from the null meter via the developed film. This program is listed in Appendix V. The computer program takes the 100 data points and plots them as a frequency

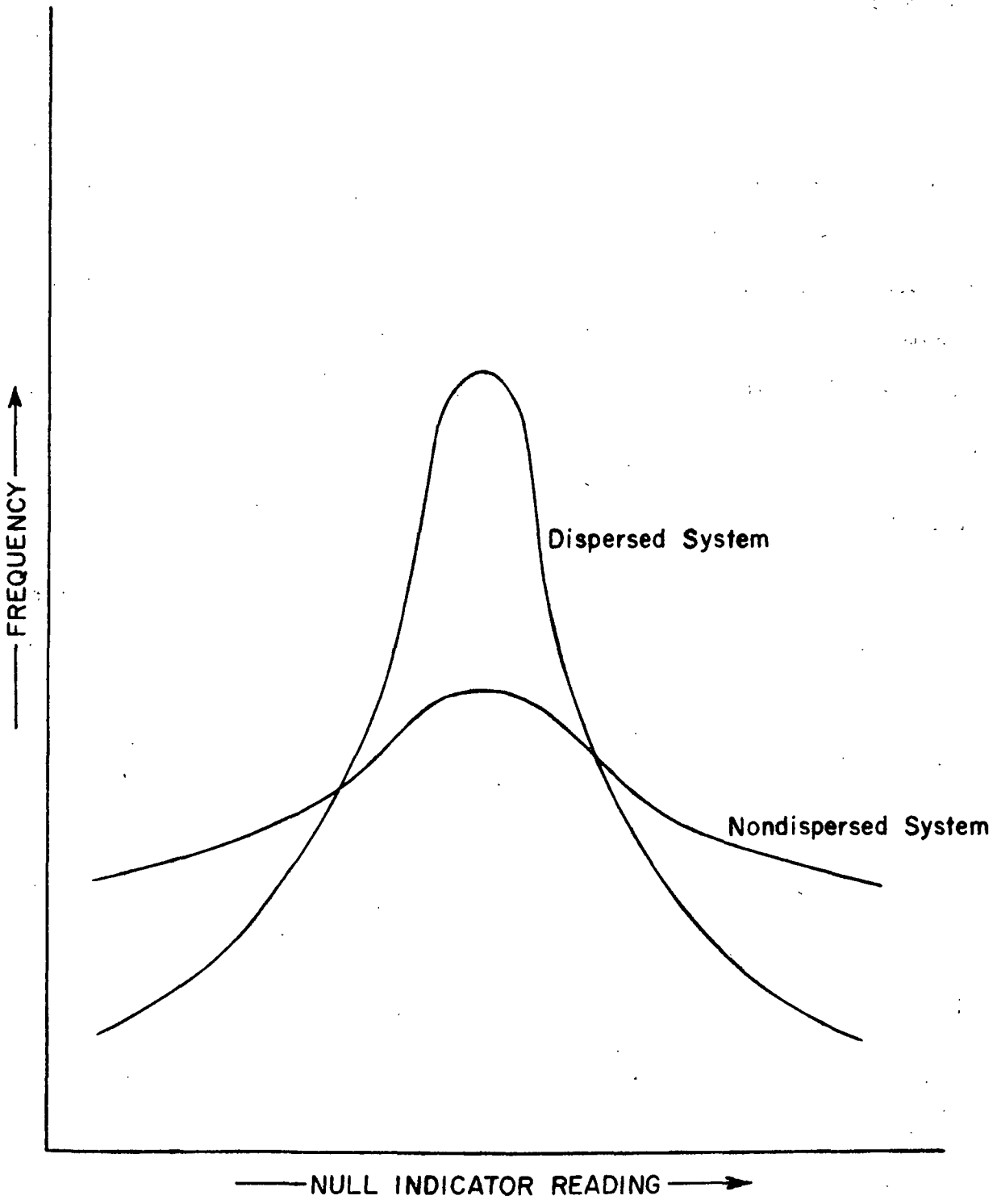


Figure 8. Frequency Distribution Curves for Dispersed and Nondispersed Systems (Idealized)

distribution, while also calculating the standard deviation of the frequency distribution. A typical set of data along with a typical computer printout is also shown in Appendix V.

All of the plots presented in this paper have been drawn as smooth curves through the data points, while not trying to connect each and every data point with the curve. It was impossible to conduct a sufficient number of test evaluations to permit a consideration of a data point as a true and absolute value. Whenever an averaged data point had an unusual error associated with it, additional test evaluations were made in order to become confident in the value plotted in the figure.

FINES-TO-FIBER

A computer program, given in Appendix VI, was written to take the data obtained from the liquid scintillation counter and calculate the percentage of fines added which were retained by the test system. Percentage fines retention is defined as the ratio of the weight of carbon-14 tagged fines attached to the fibers* to the total weight of carbon-14 tagged fines added to the system. And so,

$$\% \text{ Retention} = 100 \times \left[1 - \frac{\text{wt. of unattached C-14 fines}}{\text{total wt. of C-14 fines added}}\right]. \qquad (2)$$

Note, however, that the weight of the carbon-14 fines is directly proportional to its radioactivity in counts per minute (cpm). Then from Equation (2),

$$\% \text{ Retention} = 100 \times \left[1 - \frac{\text{cpm of unattached C-14 fines}}{\text{cpm of C-14 fines added}}\right]. \qquad (3)$$

*This number includes fines attached to system fiber plus fines not passing through the sample port. This background value was generally about 40% for 255 rpm and 20% for 585 rpm (see Appendices XIX and XX).

Before applying Equation (3), the radioactivity in cpm for all samples was corrected for background counts and converted to a common sample size of 2.0 ml and a common dilution volume of 1.0 liter.

RESULTS AND DISCUSSION

This Results and Discussion section will consist of a presentation of test results for the fiber-to-fiber studies and for the fines retention studies. Supportive studies and equipment evaluations will be discussed at points where they are of importance to the understanding of test results.

FIBER-TO-FIBER STUDIES WITHOUT FINES

The variables evaluated on the fiber-to-fiber interactions and discussed in this section include electrolyte type, electrolyte concentration, polymer type, polymer concentration, agitation conditions, and pH conditions.

STUDIES WITH ELECTROLYTE ONLY

Electrolytes evaluated included NaCl, $CaCl_2$, and $LaCl_3$. All of the electrolyte concentrations reported have been calculated on the basis of volume dilution of master solutions. Samples of the slurry supernatant were submitted for an analytical analysis of electrolyte concentration, and were found essentially to agree with dilution concentrations.

Results obtained for the three test electrolytes added to the fiber-to-fiber systems are presented in Fig. 9. Tabulated data for these systems are located in Appendix VII. The curves of Fig. 9 were drawn with some bias, since it had been shown previously by Walkush (5) and Williams (13) that electric double layer compression via simple electrolytes resulted in curves of the general shape used here. The results found in the current study fall on these idealized curves within the experimental scatter of the data, supporting the view that the curves can be drawn through the data point pattern without connecting each and every data point. From these data it is apparent

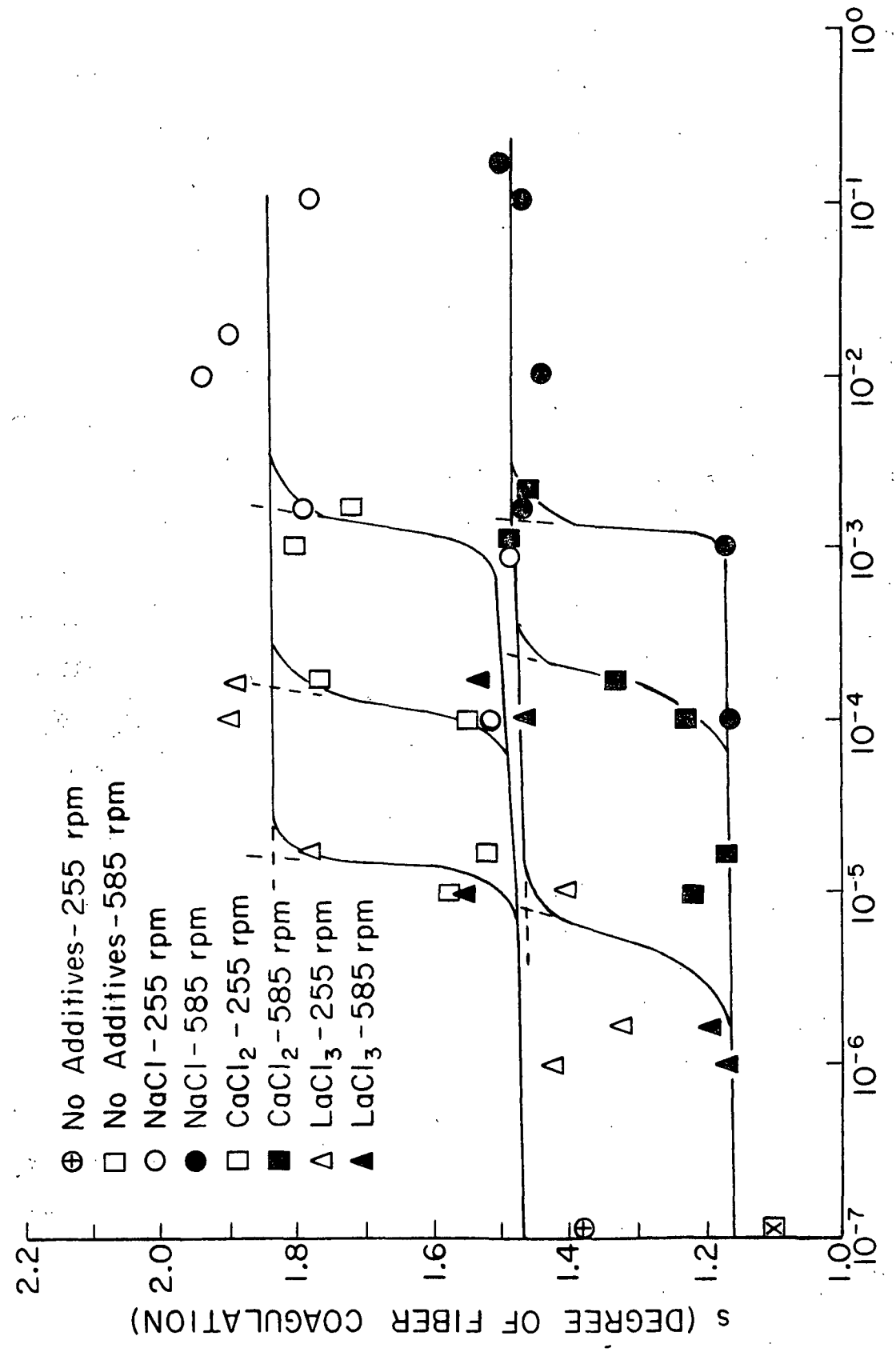


Figure 9. Cellulose Fiber Coagulation as a Function of Cation Concentration and Impeller Speed

that the valence of the cation significantly affects fiber coagulation, i.e., the higher the cation valence, the lower the concentration required to obtain the same degree of coagulation. This finding is in concurrence with the Schulze-Hardy rule which predicts that the concentration required to coagulate a particle system decreases with the inverse sixth power of the valence.

Fiber coagulation was shown to be related to the individual electrolyte (cation) concentrations. When a critical concentration of electrolyte was reached, the fibers proceeded from a noncoagulated state to a coagulated state. Once this electrolyte concentration had been reached, no additional electrolyte had any effect on the degree of coagulation of the fibers. These critical concentration values were of the order of 5×10^{-3}M for Na(+1), 3×10^{-4}M for Ca(+2), and 1 to 5×10^{-5}M for $LaCl_3$. Typically, the critical concentrations for hydrophobic colloids lie between 2.5×10^{-2}-1.5×10^{-1}, 5×10^{-4}-2×10^{-3}, and 1×10^{-5}-1×10^{-4} moles per liter for mono-, di-, and trivalent cations, respectively (86).

The critical concentrations for the present fiber systems are lower than the expected values for hydrophobic colloids coagulated by sodium and calcium, while lanthanum is well within the anticipated range. There are two possible explanations for the lower concentrations. First, it was pointed out by Sparnaay (87) that the critical concentrations for flat plates should be more than for small cylinders, indicating that elongated particles like fibers and fines could have lower critical concentrations than theoretically calculated.

Secondly, as suggested by Walkush (5), the coagulation is controlled by a relatively deep secondary energy well that can exert its influence at low concentrations of cations, if the particles are large or of irregular shape. Generally, the potential energy curves for coarse particles have a comparatively deep energy well associated with them at large separation distances, resulting from the gradual decay of the attractive potential. This type of coagulation is highly reversible since there is no potential barrier to overcome as is the case for true coagulation. Although the work of Walkush concluded that fines retention was reversible upon increased agitation and that the secondary minimum influence was important, the current study cannot argue definitely on the influence of the secondary minimum on fiber-to-fiber interactions as affected by simple electrolytes.

There is a lower degree of coagulation for the fiber systems as the agitation is increased, indicating the possibility of reversible fiber interactions. However, it is impossible to separate the reversibility of the fiber coagulation from the changes in flow patterns of fibers as seen by the light probe in going from 255 to 585 rpm. Because of this flow pattern problem associated with the light probe, it is not possible for the current study to come to any definite conclusions on the question of the secondary minimum influence on fiber-to-fiber coagulation.

The study completed by Walkush (5) evaluated the effects of NaCl, $CaCl_2$, and $LaCl_3$ on fines-to-fiber interactions. Walkush's corrected retention isotherm for the three systems is presented in Fig. 10. On comparing the current results of Fig. 9 with Walkush's results, it is concluded that the fiber-to-fiber and fines-to-fiber interactions were influenced to the same degree by the action of NaCl, $CaCl_2$, and $LaCl_3$. Not only are the curve

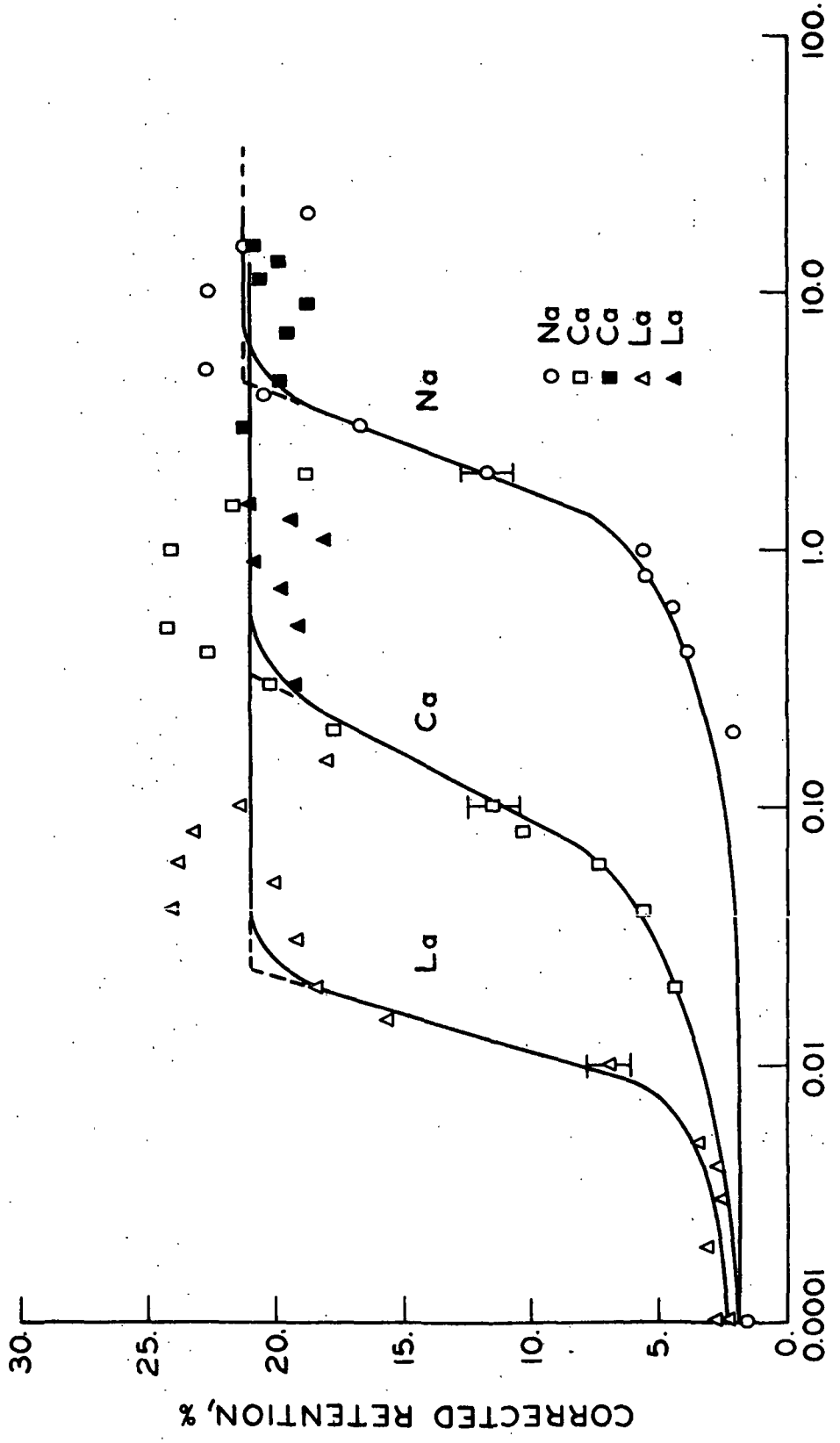


Figure 10. Fines Retention Data of John Walkush as a Function of Cation Concentration and Cation Species Type

shapes identical for both systems, but also the critical electrolyte concentrations are almost identical for the respective electrolytes: current Na(+1) of 5×10^{-3}M to Walkush Na(+1) of 4.5×10^{-3}M, current Ca(+2) of 3×10^{-4}M to Walkush Ca(+2) of 3.3×10^{-4}M, and current La(+3) of 1 to 5×10^{-5}M to Walkush La(+3) of 2.3×10^{-5}M. These critical concentrations are defined at the point where the linearly extrapolated portions of the interaction curves intersect as seen in Fig. 9 and 10.

Also of major importance is the effect that the two agitation conditions had on the fiber coagulation systems. For the Na(+1) and Ca(+2) test systems, the two agitations produced fiber-to-fiber interaction curves of identical shape, varying in neither the maximum change of fiber coagulation nor in critical concentration. However, for the high agitation condition with $LaCl_3$, the critical concentration occurred at a lower concentration than for the low agitation condition. Increased agitation can influence the cluster formation tendencies in two ways: first, by increasing particle collision frequency, and second, by increasing disruptive turbulence forces (36-38). The NaCl and $CaCl_2$ systems were functioning in such a way that neither the increased turbulence nor the increased number of particle collisions was affecting the system coagulation. On the other hand, $LaCl_3$ was a powerful enough coagulant that the increased collision factor became a greater influence and less electrolyte was required to achieve the same degree of coagulation. If the turbulence factor had been more important, then the intensity of the coagulation would have changed and not the cation concentration required to complete coagulation.

The shape of the fiber coagulation curves is of a shape typical of other hydrophobic colloids: arsenic trisulfide (88), polystyrene (89), and silver

halides (90). The curve region where cation concentration dependency was seen is generally associated with gradual increases in coagulation as the double layer repulsions are negated by cation addition. The cation independent region was observed as the system underwent rapid coagulation at a point where the repulsive forces were reduced to a value less than the attractive forces. After achieving the rapid coagulation of the system, and in the absence of specific cation adsorption, additional cation had no effect on the coagulation tendency of the fiber. If specific cation adsorption were taking place, the cellulose could go through a stage of charge reversal, once again setting up a dispersive electric double layer repulsion, resulting in fiber redispersion. This charge reversal on cellulose has been observed by Goring and Mason (91) for Th(+4) addition, as well as Thode and Htoo (92) and Ostwald and Lorenz (93) for Al(+3) addition. Charge reversal was not a factor for the current system as no redispersive tendencies were found upon additional cation doses after the rapid coagulation period.

It is interesting to note that the maximum degree of coagulation was the same for all three electrolytes, indicating that the electrolyte effect was controlled by some common fiber or system quality. Walkush (5) found the same occurrence for his carbon-14 fines-to-fiber interactions, explaining the result in terms of a dynamic equilibrium being established between fines-to-fiber formation and destruction, with agitation being the important controlling factor for fines-to-fiber destruction. The tendency to form fines-to-fiber clusters was dependent on fiber consistency, agitation rate, and electrolyte environment. This dynamic equilibrium proposed by Walkush for his fines retention work was also operating for the current fiber-to-fiber systems under the influence of simple electrolytes.

STUDIES WITH POLYMER ONLY

Fiber-to-fiber interactions were monitored as a function of polymer type, polymer concentration, agitation conditions, and pH conditions. All polymer concentrations reported are volume dilution concentrations based on the amount of polymer by weight added to the fiber slurry, and are given in units of parts per million (ppm) by weight. The results for the cationic studies are shown in Fig. 11, for the anionic study in Fig. 12, and for the nonionic study in Fig. 13. Tabulated data for these figures can be found in Appendix VIII.

Single curves were used to depict results obtained for pH 5, 7, and 9, since the evidence found during the entire program supported no pH effects on fiber-to-fiber interactions. All curves presented in Fig. 11-13 are for fiber batch I, except where some 585-rpm data for the anionic polymer are labeled for fiber batch II. All subsequent data presented in this paper are for batch II fiber.

All of the fiber-to-fiber systems showed no effect of pH over the pH range of 5 to 9. The cationic polymer exhibited a maximum degree of flocculation at 40 ppm for low agitation conditions and at 10 ppm for high agitation conditions. The anionic polymer showed a much broader response of the increase in the degree of fiber flocculation to concentration at 255 rpm than did the cationic polymer, while no significant increase in flocculation was found at 585 rpm. The apparent increase for 30 ppm anionic polymer at pH 7 and 585 rpm was concluded not to be significant after retrials with batch II fiber (dark hexagons of Fig. 12). The nonionic polymer system responded in much the same way as did the anionic polymer system, showing a broad increase in the degree of fiber flocculation at low agitation, while showing no increase at the elevated agitation.

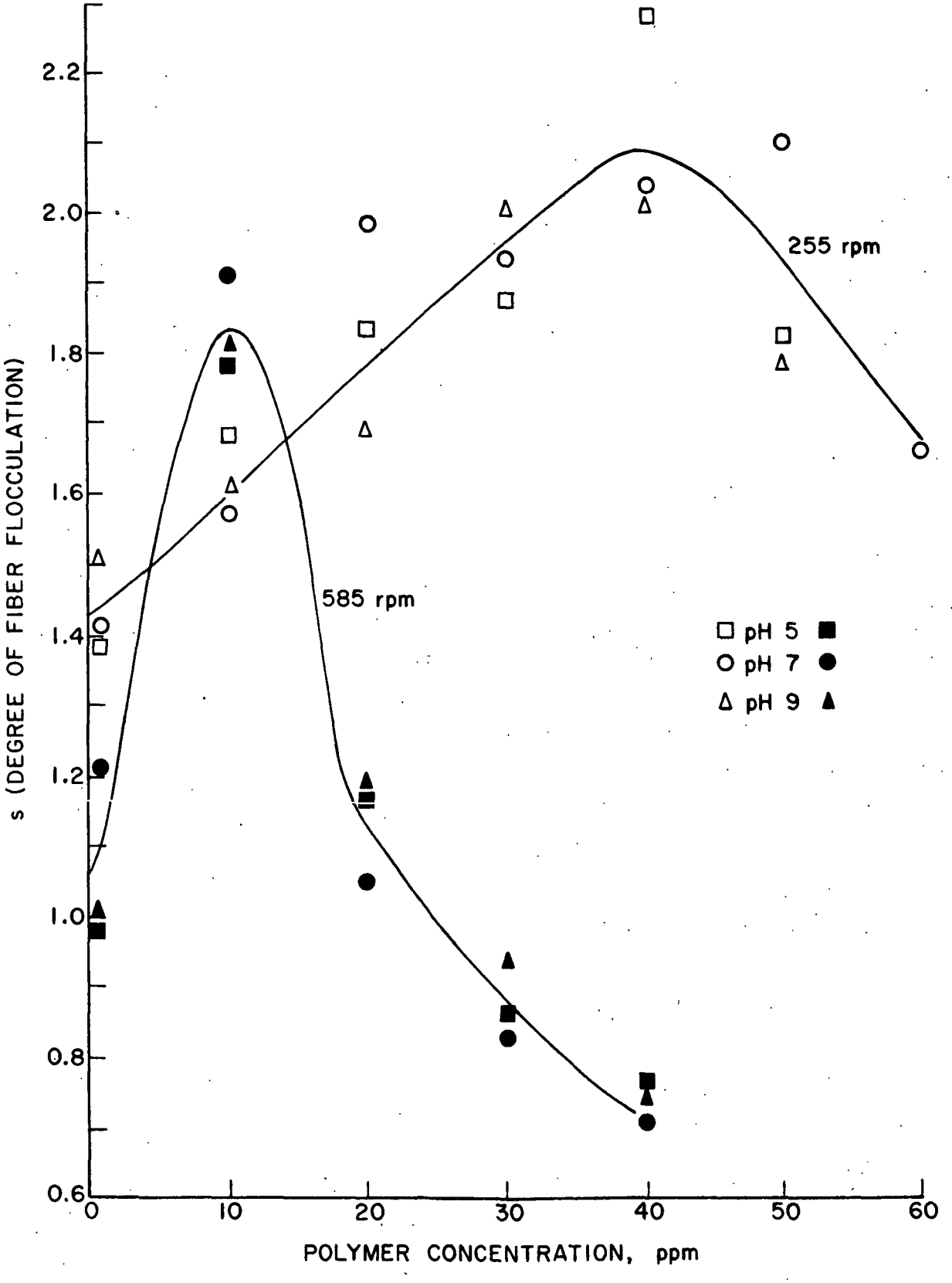


Figure 11. Cellulose Fiber Flocculation as a Function of Cationic Polymer Concentration, System pH, and Impeller Speed

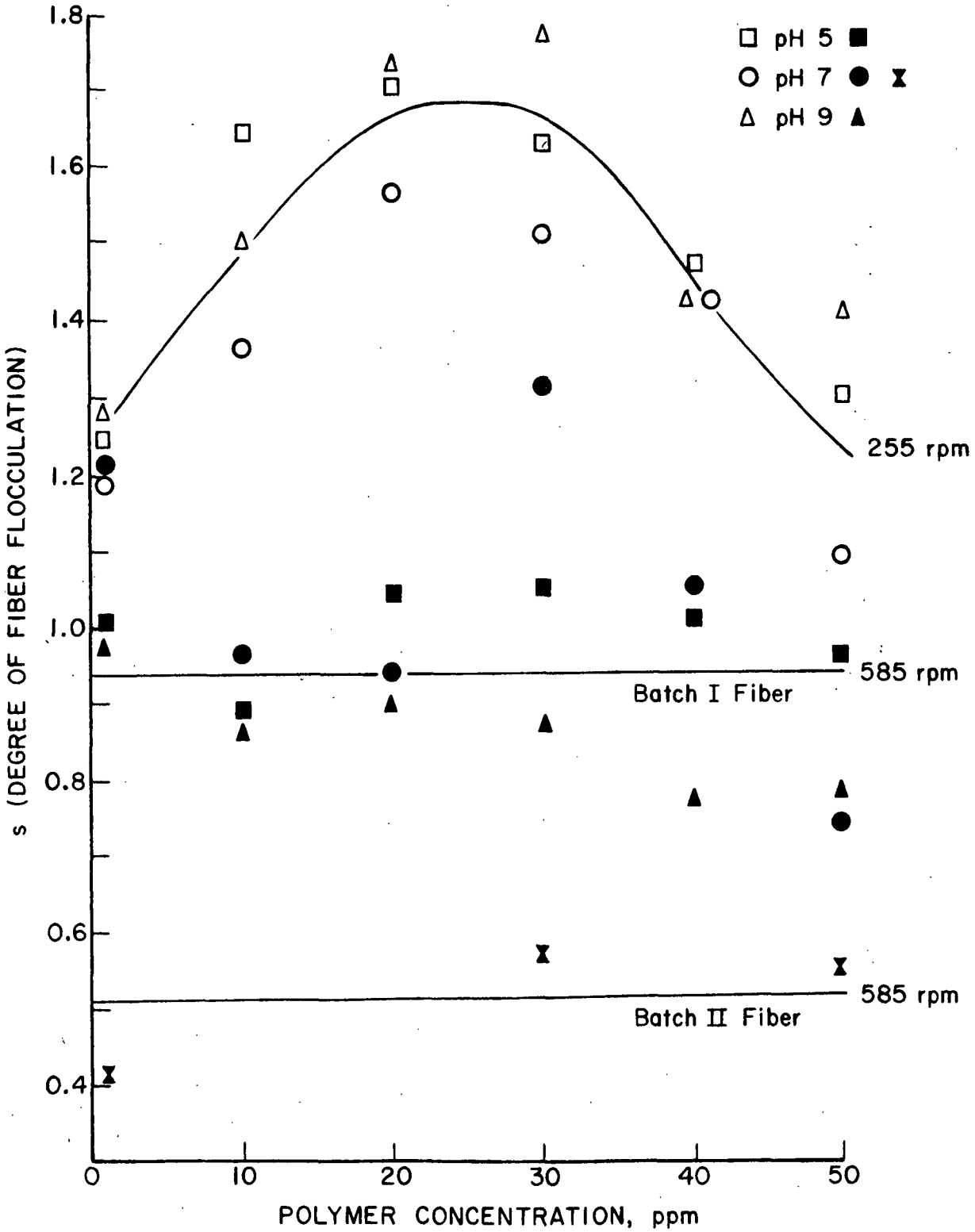


Figure 12. Cellulose Fiber Flocculation as a Function of Anionic Polymer Concentration, System pH, and Impeller Speed

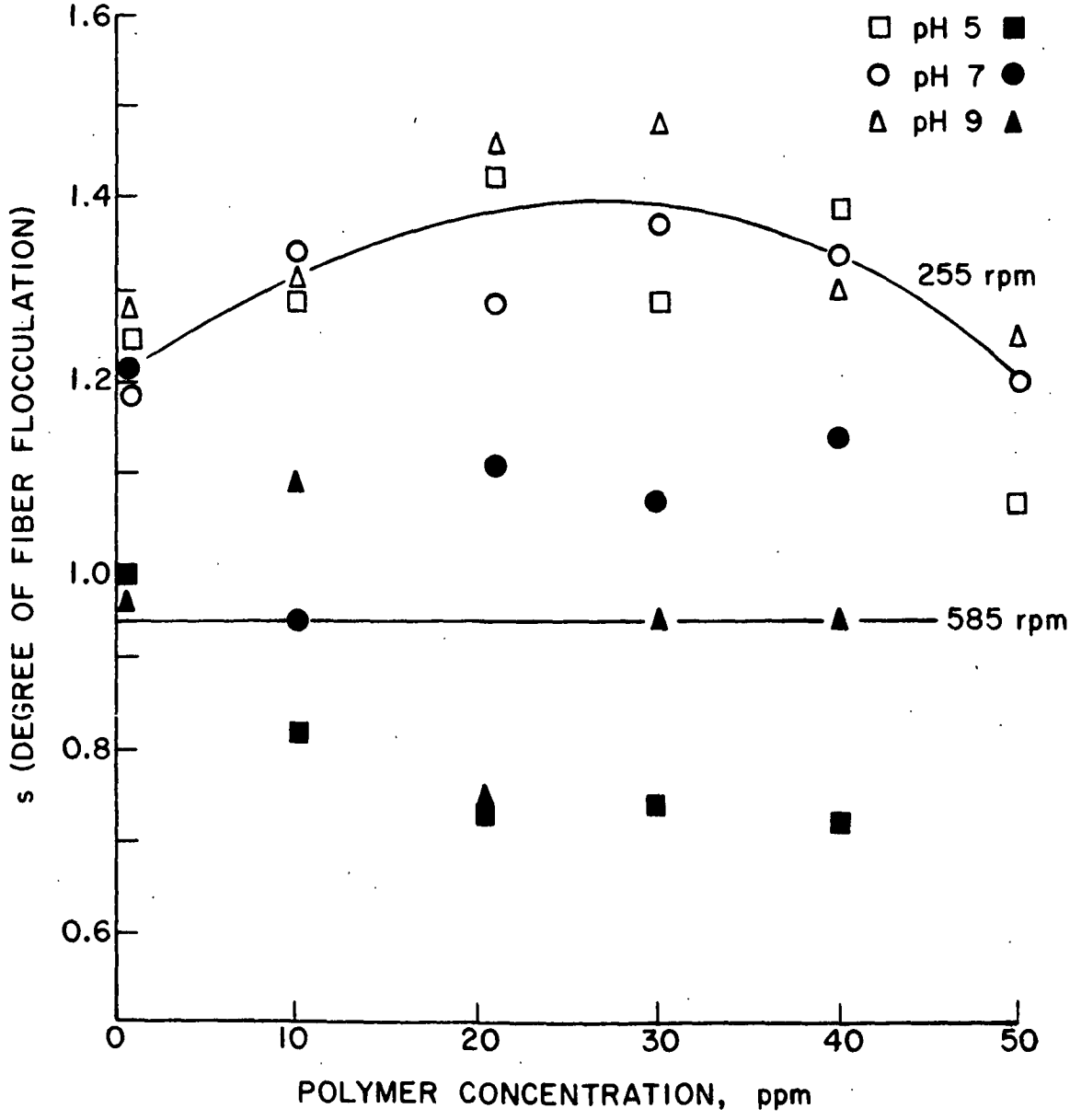


Figure 13. Cellulose Fiber Flocculation as a Function of Nonionic Polymer Concentration, System pH, and Impeller Speed

The lack of pH dependence for the polymers by the fiber-to-fiber interactions is surprising since the degree of ionization of the tertiary amine group of the cationic polymer and the carboxylic acid groups of the anionic polymer should depend on system pH over the pH range 5.0 to 9.0. This functional group pH dependence would suggest that polymer-fiber interactions would also be pH dependent, and so polymer flocculating power would be pH dependent. For similar reasons, it was expected that the uncharged functional groups of the nonionic polymer would not be pH dependent. It is felt that any pH influences in this system are thus probably outside the sensitivity of the fiber optics light probe.

Agitation effects were very important in this polymer-only study. The cationic polymer was a better flocculant at increased agitation, i.e., less polymer was required to flocculate the system as the agitation was increased from 255 to 585 rpm. Both the nonionic and anionic systems acted as flocculants at low agitation, but did not flocculate the fiber-to-fiber system to any degree at the high agitation.

There can be three influences of agitation on polymer flocculation. LaMer and Healey (94) have suggested that as agitation is increased, the collision frequency of particles increases, resulting in more collisions of sufficient energy for the particles to overcome potential energy barriers and remain attached. Thus, less polymer would be required to achieve a similar degree of flocculation at high agitation than at low agitation. At the same time, the increased agitation can disrupt already formed fiber clusters, resulting in a system where stronger polymer adsorption forces, i.e., polymer bridges are required to maintain fiber flocculation.

The amount and type of agitation can also influence the degree of flocculation achieved by a particular polymer system. Fleer (71) has demonstrated that the manner by which a AgI-PVA slurry was mixed affected the AgI flocculation. Under certain mixing conditions, the PVA polymer was able to attach more uniformly and to more particles, thus becoming a better flocculant. If better polymer distribution was achieved at elevated agitations, then less polymer could maintain a certain degree of flocculation at high agitations than at low agitations.

In the case of the cationic polymer, the agitation influences resulting in increased collision frequency of particles and more optimum mixing conditions were overriding the disruptive influences of increased agitation, since less polymer was required at the 585-rpm test case than at 255 rpm. It was beyond the scope of this work to establish whether the increased collision mechanism or the optimum mixing mechanism was of more influence.

For the anionic and nonionic polymers, it is clear that the disruptive forces of increased agitation were sufficient to prevent the polymers from flocculating the cellulose fibers at the 585-rpm test conditions.

The ability of the cationic polymer to flocculate the fibers at elevated agitation, whereas the anionic and nonionic polymers were unable to do so, points out the importance that polymer charge plays in flocculating cellulose fibers. Also, the cationic polymer was a more effective flocculant than was the anionic or nonionic polymers at low agitation. These results are as would be expected, since the positively charged cationic polymer would adsorb more strongly to the negative cellulose than either the negatively or noncharged polymers.

Perhaps, it is surprising that there was any flocculation found at all for the anionic and nonionic systems, since the polymers are generally used with electrolyte so that the negative character of cellulose will be reduced or eliminated. Apparently, for the current system without electrolyte, there were enough active centers on the cellulose surface and the like charge centers were far enough apart for the anionic and nonionic polymers to adsorb, such that some increase in flocculation was recorded. It is probable that the anionic and nonionic polymers interact with cellulose through hydrogen bonding.

Polymer adsorption data to be presented in a later section demonstrated increasing cationic polymer adsorption as the polymer concentration was increased. However, the analytical method employed was not sensitive enough to determine the amounts of anionic or nonionic polymer adsorbed by the cellulose fibers at the very low polymer concentrations used. This finding is in agreement with the fact that the anionic and nonionic polymers were much poorer flocculants than the cationic polymer.

Fischer (95) has proposed a model for nonionic polymer flocculation based on a concept different from hydrogen bonding. The mechanism, termed a mixing model by Bagchi (96), occurs at low coverage by polymer when the polymer coverage layers mix on particle approach. If the mixing of polymer surface layers occurs with a net increase in free energy, then repulsion of the particles will take place. If Van der Waals attractive forces are greater than the repulsive forces, then the mixing of the polymer chains will be sufficient to hold system particles together. The current study did not attempt to establish the specific type of nonionic flocculation mechanism.

For all systems where an increase in flocculation was found, the flocculation curves exhibited three distinct regions: (1) a region of gradual flocculation increase as polymer concentration was increased, (2) a region of maximum flocculation, and (3) a region of gradual flocculation decrease as polymer concentration was increased past the maximum flocculation point. This curve shape is that shape typically found for systems flocculated via a polymer bridging mechanism (94,97).

This flocculation behavior would also be expected if the polymer were affecting charge parameters of the cellulose. As the negative charge of the cellulose was reduced an increase in flocculation would be observed, with the maximum flocculation found at a point of zero cellulose charge. Then as the cellulose charge was reversed becoming more and more positive, there would be an increased dispersion of the fibers. It is possible that the cationic and anionic polymers were working through both bridging and charge effects. However, it is unlikely that the nonionic polymer was working on cellulose flocculation via charge effects, but rather through the bridging mechanism only.

Finally, it is important to note that all three test polymers did exhibit a redispersive tendency on the test fibers. This observation is an important one, because of the importance of the fiber dispersion on sheet formation problems found in mill situations. As will be discussed throughout this report, if conditions are well chosen, it may be possible to achieve both good fines retention and good fiber dispersion.

STUDIES WITH BOTH ELECTROLYTE AND POLYMERS

This section of the current study will be concerned with the total degree of flocculation brought about by first collapsing and/or compressing the diffuse electric double layer of the fibers with a suitable electrolyte, followed by flocculation of the fibers by addition of the test polymer. Having determined in the electrolyte-only studies that $LaCl_3$ was the most efficient electrolyte coagulant, $LaCl_3$ was selected for the electrolyte-polymer program. Enough $LaCl_3$ (1×10^{-4} M) was added to the fiber slurry to effectively coagulate the fibers, followed by polymer addition. Based on the evidence of no pH effects in the polymer-only programs, it was decided to evaluate only at the pH range limits, 5 and 9. All systems were evaluated at both the 255 and 585-rpm test agitations. The results of the cationic polymer systems are presented in Fig. 14, of the anionic polymer systems in Fig. 15, and of the nonionic polymer systems in Fig. 16. Tabulated data of the results given in these figures can be found in Appendix IX.

Once again there were no differences in system behavior, when the pH was changed from 5 to 9. Also, note that the test systems which did show an increase in flocculation on polymer addition exhibited the increase above that coagulation which the $LaCl_3$ electrolyte had already produced. The fiber networks formed upon $LaCl_3$ addition were made more extensive with the addition of polymer. On systems where the polymers produced an effect, the degree of cluster formation on large polymer additions was reduced to values even lower than the electrolyte-only value. Thus, increased polymer addition can show a dispersive effect.

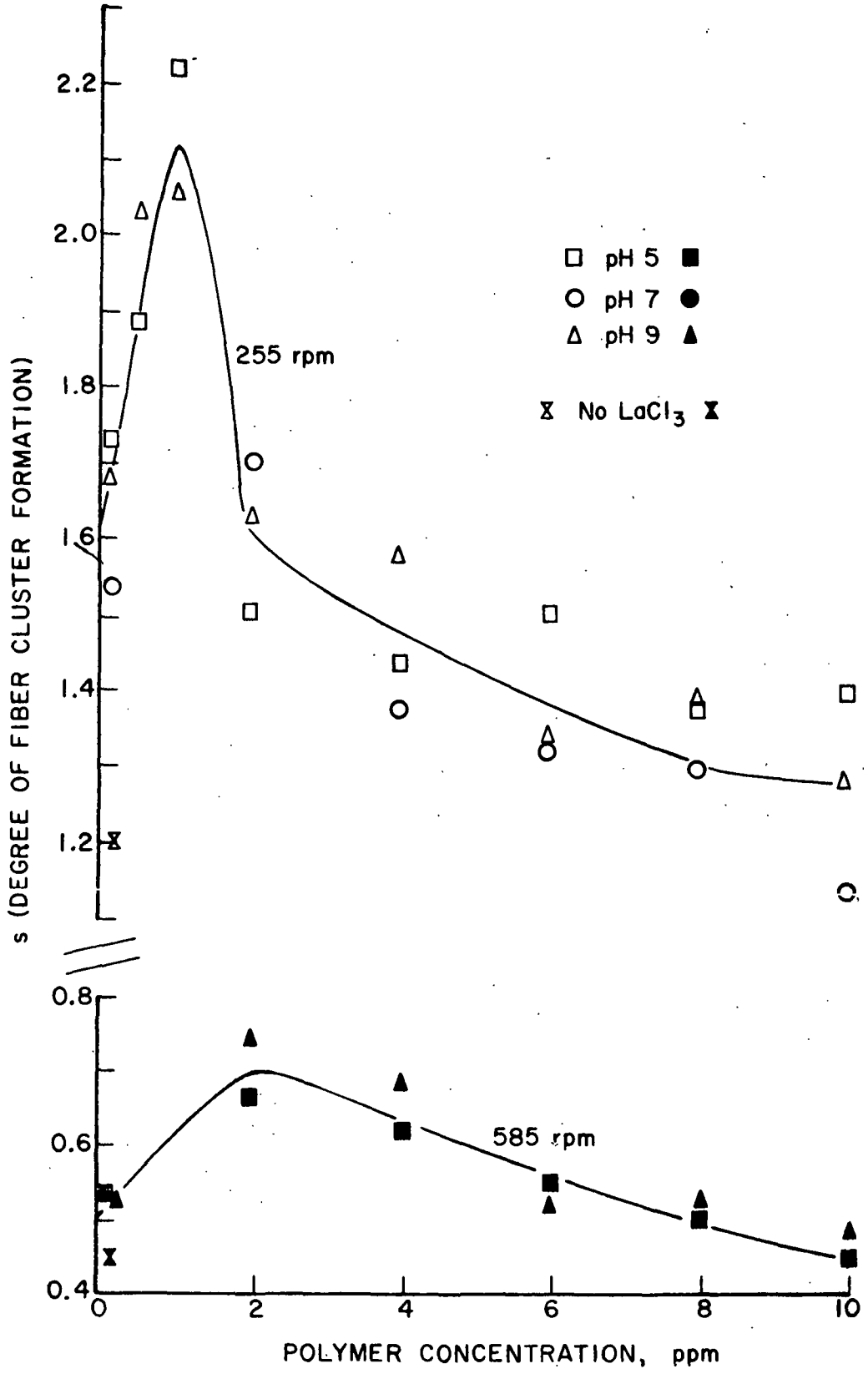


Figure 14. Cellulose Fiber Interactions as a Function of Cationic Polymer Concentration, $LaCl_3$ Electrolyte, System pH, and Impeller Speed

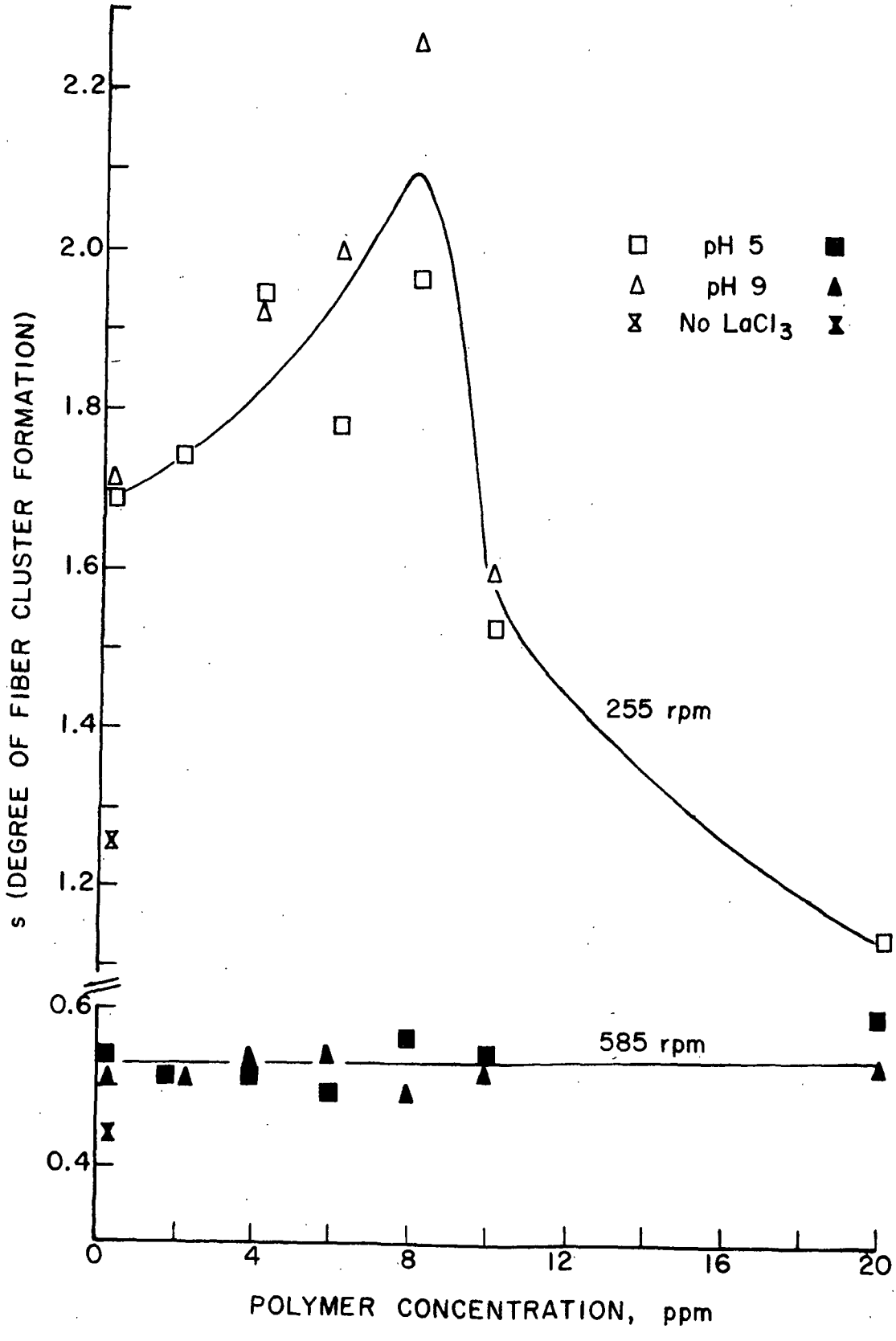


Figure 15. Cellulose Fiber Interactions as a Function of Anionic Polymer Concentration, $LaCl_3$ Electrolyte, System pH, and Impeller Speed

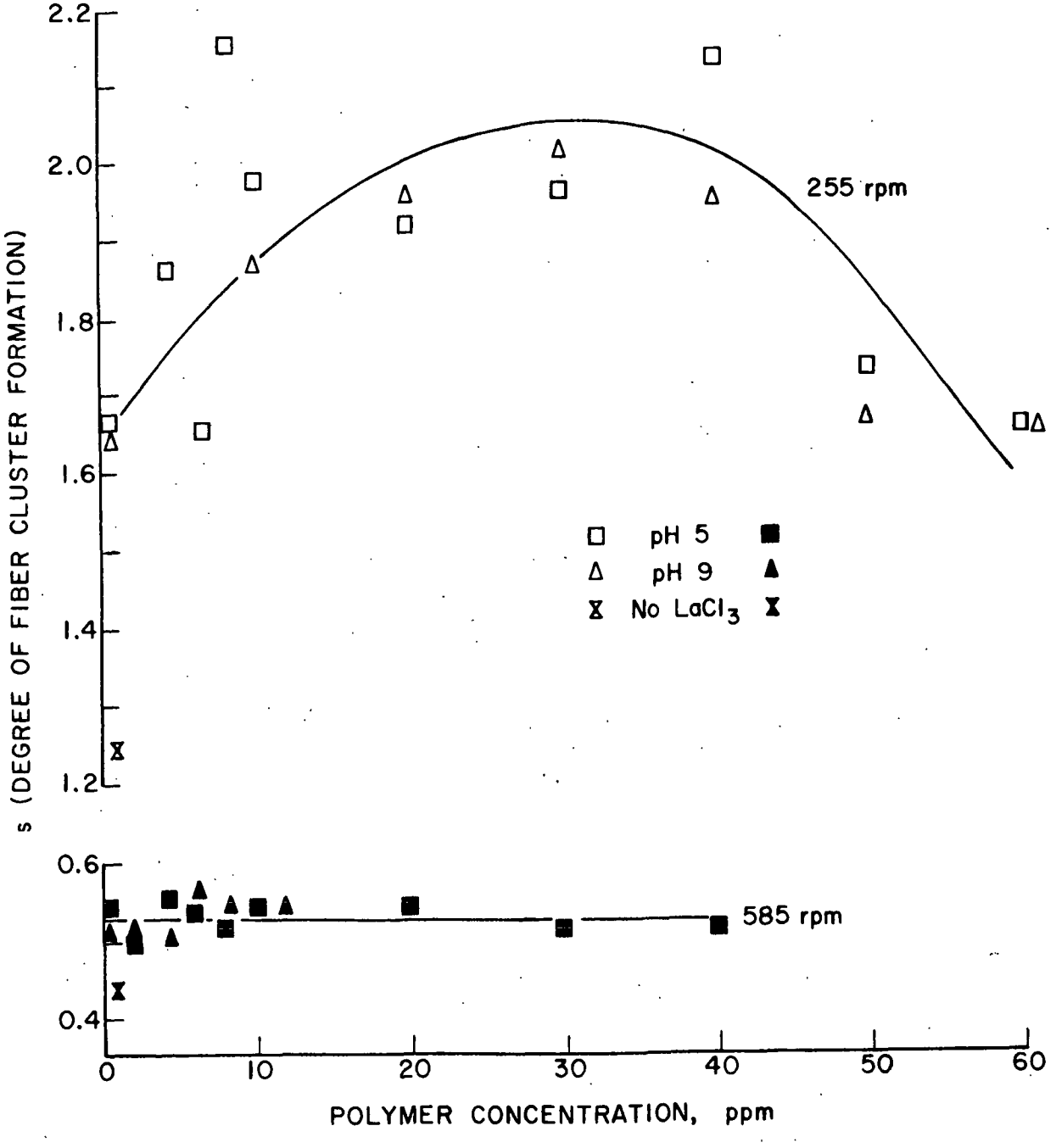


Figure 16. Cellulose Fiber Interactions as a Function of Nonionic Polymer Concentration, $LaCl_3$ Electrolyte, System pH, and Impeller Speed

On comparing these $LaCl_3$-polymer data to the polymer-only data, it is noted that the cationic polymer at both low and high agitations reached its maximum degree of flocculation at a lower polymer concentration with the electrolyte than without the electrolyte (Fig. 11 and 14). There are two explanations for this observation. First, the electrolyte has enabled system particles to approach more closely together by reducing the double layer influence, resulting in an increased likelihood of polymer bridges being formed. Therefore, less polymer would be required to flocculate a system under the influence of electrolyte than without electrolyte. Second, by starting with fibers already coagulated with electrolyte, the added polymer encounters larger particles than without electrolyte. The action of the electrolyte in forming larger fiber clusters is to reduce the surface area associated with the cellulose fibers. LaMer, et al. (98) have demonstrated that a lower flocculant concentration is required to achieve maximum flocculation as the surface area of the suspension particles is lowered.

A similar trend as described above for the cationic polymer was also found for the low agitation anionic polymer system. Similar explanations for the double layer compression and surface area effects would hold equally as well for the anionic polymer as for the cationic polymer.

The shape of the anionic flocculant curve with electrolyte is slightly altered from the curve without electrolyte. The effective polymer flocculating concentration was more narrow with $LaCl_3$ than without $LaCl_3$, showing a general increase in flocculating power up to 8 ppm polymer, followed by a very strong dispersive action as polymer concentration was increased. The $LaCl_3$ has significantly reduced the electric potential associated with the

cellulose, making it much easier for the anionic polymer to adsorb to the active sites of the cellulose, probably through some type of hydrogen bonding. Thus, the anionic polymer became a much better flocculant under the influence of the $LaCl_3$, and in fact behaved very much like the cationic polymer at low agitation (Fig. 14). It would also be possible that the charge effects of the system were altered to a significant level, such that surface charges were reestablished and the fibers began to repel each other. Either explanation could be valid for the curve shapes obtained in this study, and in fact both the polymer effects and the charge effects are probably of importance in the $LaCl_3$ anionic polymer system.

The anionic polymer showed no tendency to form fiber clusters at high agitation even with the $LaCl_3$ present. The increased polymer-fiber interactions allowed by the effects of the double layer compression by $LaCl_3$ were not intense enough to overcome the turbulence effects at high agitation.

The nonionic polymer systems at low agitation showed almost identically shaped curves with and without $LaCl_3$, both having maxima in the degree of flocculation at about 30-ppm polymer (Fig. 13 and 16). However, this increase in flocculation with $LaCl_3$ was more intense than for the polymer without electrolyte. This increase in the degree of fiber flocculation indicates that the $LaCl_3$ increased the flocculation power of the nonionic polymer as it had for the cationic and anionic systems.

The nonionic system did not show the strong dispersive tendency at low shear as had the cationic and anionic polymers. This fact indicates that a polymer without the ability to influence cellulose charge structure, is not likely to exhibit strong interactions with the cellulose fibers at

the concentrations examined. The nonionic polymer system with $LaCl_3$ at high agitation showed no flocculating increases at either pH 5 or 9, again indicating a breakdown of fiber-polymer interactions under the increased turbulence.

SUPPORTIVE STUDIES FOR FIBER-TO-FIBER INTERACTIONS

The results of a series of studies required as support for the fiber-to-fiber evaluations are now presented. These studies involve the determination of the fiber consistency used throughout the program, impeller positioning and rpm determination, system reproducibility, impeller cutting action determinations, time of agitation determinations, accelerated aging study, and polymer adsorption work.

(1) The consistency of a fiber slurry plays an important role in the degree of fiber and fines interactions (5,69). Walkush (5) investigated the effects of fiber consistency variations on fines retention, finding that fines retention increased with fiber consistency increases. Muhonen (69) observed that only a narrow range of fiber consistencies were found to supply reproducible data using the fiber optics light probe. Too low consistency fiber samples tended to settle in the test vessel unless a high agitation was used, resulting in a very low variance in reflected light intensity. A too large consistency required a high agitation rate in order to keep the fiber moving in the test vessel. Thus, it became important to determine the most useful fiber consistency for the current study.

Fiber consistencies evaluated included 0.1, 0.5, and 1.0% of oven-dried fiber per 100 grams of total slurry weight. Sensitivity at the 0.1% level in the light probe readings was not adequate for experimental

requirements, while system reproducibility was better at the 0.5% level than at the 1.0% level. Therefore, the fiber consistency established for this program was 0.5 gram of oven-dried fiber per 100 grams of total slurry weight. This 0.5% consistency determination is presented in greater detail in Appendix X.

(2) It was also known that the hydrodynamic agitation conditions of the slurry could affect the manner to which the fiber optics light probe observed fiber-to-fiber interactions. Meyer (99) suggested that the position of the agitator impeller, i.e., the position of the impeller with respect to the light probe, could affect the intensity of reflected light coming from the fibers as seen by the light probe. Chiu (43) observed a strong dependence of impeller angle on the intensity of the reflected light as picked up by the light probe. Thus, it was important for the impeller system of the present study to be characterized in such a way that its position with respect to the light probe could be reproduced for each test evaluation. The impeller position was selected so that maximum system reproducibility was achieved. Throughout this entire program, an angle of 72.5° was used for the angle at which the impeller shaft entered the test slurry. By maintaining the angle at exactly 72.5° for each test situation and realizing that the impeller was at a fixed position on a rigid shaft, it was possible to reproduce impeller position with respect to the light probe very accurately. An exact description of the impeller positioning along with a complete description of the angle determination can be found in Appendix XI.

(3) Fiber entanglement and fines retention can be influenced greatly by the degree of agitation of the test slurry (5,43,44). Therefore, two agitation conditions were selected to evaluate all fiber-to-fiber and fines-to-fiber interactions. These two conditions were chosen by plotting the degree of fiber cluster formation versus agitation rates and selecting two agitation rates, one where it was thought fiber entanglements were important and one where it was thought entanglements were much less important. This plot is presented in Fig. 17 with tabulated data given in Table III.

TABLE III

EFFECT OF IMPELLER SPEED ON FIBER CLUSTER FORMATION

System Number	Impeller Speed, rpm	Degree of Fiber Cluster Formation	Averages
1-66-1A	110	9.22	9.01 ± 0.30
1-66-2A		8.79	± 3.4%
1-67-1A	160	6.21	7.35 ± 1.60
1-67-2A		8.48	± 21.8%
1-67-3A	200	7.31	7.02 ± 0.42
1-67-4A		6.72	± 5.9%
1-68-1A	255	8.41	7.88 ± 0.76
1-68-2A		7.34	± 9.6%
1-68-3A	305	7.62	7.09 ± 0.76
1-68-4A		6.55	± 10.7%
1-69-1A	350	8.30	7.69 ± 0.87
1-69-2A		7.07	± 11.3%
1-69-3A	405	4.65	6.41 ± 2.49
1-69-4A		8.17	± 38.8%
1-70-1A	460	4.39	4.58 ± 0.27
1-70-2A		4.77	± 5.9%
1-70-3A	525	3.31	3.13 ± 0.26
1-70-4A		2.94	± 8.4%
1-71-1A	585	2.61	2.73 ± 0.17
1-71-2A		2.85	± 6.2%

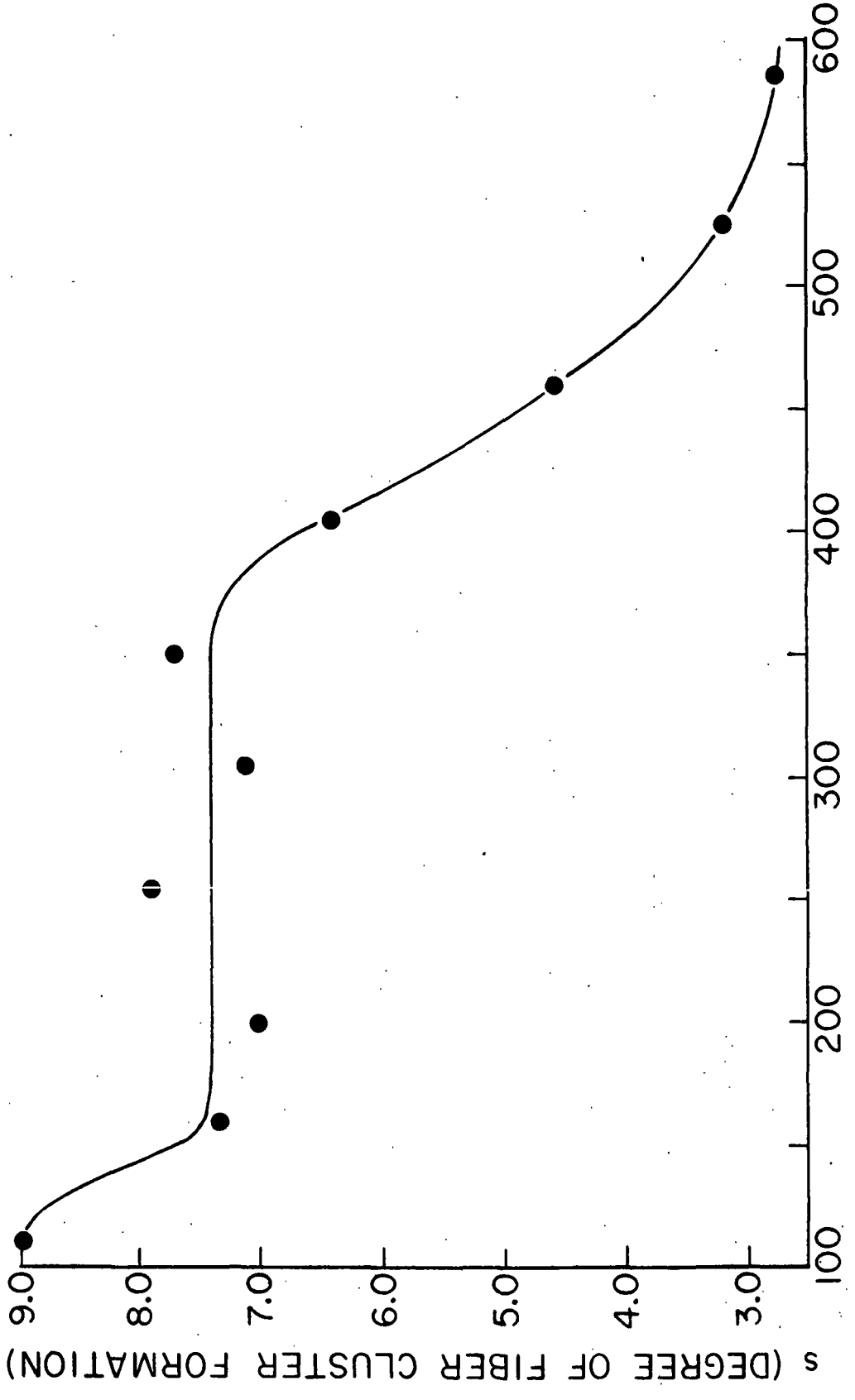


Figure 17. Effect of Agitation Speed on Fiber Cluster Formation

The results of this study have been presented here instead of in an appendix, because there are some important observations concerning the data obtained. First, the shape of the curve is significant in that it shows an initial decrease in cluster formation from 110 to 175 rpm, followed by a significant area of the curve from 175 to 350 rpm where the increase in rpm did not influence the degree of fiber cluster formation. Then from 350 to 585 rpm there was a steady decrease in fiber interactions as the rpm values were increased. Notice also from data of Table III that the points where the curve shows its bend points (160 and 405 rpm) exhibited a very large error limit, much greater than for any other experimental points.

It is felt that this study lends support for the contention that observations made by the light probe are indeed indicative of fiber interactions, and are not solely a result of changing flow patterns. While on the plateau region of the curve, the light probe is observing fiber interactions which are not influenced over a very substantial area of agitation change. Thus, fiber interactions observed over this fairly broad plateau of agitation are being influenced more by colloidal factors than by hydrodynamic conditions.

The large error limits at points where the fiber interactions are changing the greatest with agitation changes, indicate that the system is undergoing some type of fluctuation. Such fluctuations would be very undesirable during a fiber-to-fiber test evaluation. Thus, the test rpm values were selected at 255 and 585 rpm, one on the plateau portion of the curve and one at an rpm where the fiber interactions have been reduced substantially.

It is felt that at least a portion of the decrease in degree of fiber interactions from the low agitation to the high agitation is a result of changing flow patterns and particle velocity profiles but, at the same time, observable colloidal changes have been monitored at both low and high agitations. This fact indicates that changing velocity profiles and flow patterns are not dominating the colloidal effects, and the fiber optics light probe is capable of observing colloidal factors on fiber-to-fiber interactions at agitation conditions as high as 585 rpm. The rpm at which the light probe is useful will certainly vary from system to system, but it is capable of measuring colloidal influences on fiber interactions.

(4) It was desired to determine the percentage error associated with the fiber-to-fiber determination. It was found during the early stages of the program that duplicate test systems could be reproduced to a maximum error of 14%, and in most cases to much better percentage errors. Any duplicate systems falling outside of this empirical 14% limit, were suspect and tested again until the error was in an acceptable range. In many test situations as many as 5 to 10 evaluations were made. A system described below demonstrates how the error limits were determined. A 7.2% error limit was determined for the reproducibility of 10 different fiber samples evaluated at a consistency of 0.5%, pH value of 7.0, and an agitation of 300 rpm, for fiber batch I. The 7.2% was determined on the basis of a standard deviation of the standard deviations. The actual experimental data and calculations are presented in Appendix XII.

(5) Meyer (84) had pointed out the possibility that the increased cutting action of the impeller blades upon increasing system agitation might be affecting the fiber-to-fiber interactions while overriding colloidal effects. A six-bladed impeller operating under the same test conditions as the three-bladed impeller gave the same degree of fiber cluster formation as seen by the light probe as did the three-bladed impeller. Thus, the possible cutting action of the impeller blades was not an important factor in the degree of flocculation index. The details of this study are presented in Appendix XIII. The observations of this study are additional evidence supporting the idea that the light probe system is measuring actual fiber-to-fiber interactions.

(6) With the 10-minute preagitation period plus the actual run time, there was concern with the influence of extended periods of agitation on the degree of fiber cluster formation. There were two types of study in this evaluation of time of agitation effects: one where the fiber-to-fiber interactions without additives were monitored over extended periods of time, and one where the interactions were monitored on a time basis while under the influence of the three test polymers as well as the test fines. In the time of agitation studies without additives, no effects were seen on the fiber-to-fiber interactions for agitation times up to 23 hours. No decreases in fiber flocculation were found for fiber-polymer systems agitated at 585 rpm for up to 45 minutes. The results of the polymer studies indicate that agitation conditions employed were not severe enough to destroy fiber-polymer-fiber bridges. The no additive results indicate that the preagitation conditions sufficiently brought the fiber networks to their equilibrium size for the test conditions, such that no changes in fiber cluster formation would

be observed during the course of a test as a result of time of agitation. The detailed data for these time of agitation studies are presented in Appendix XIV.

(7) The possibility of an aging effect upon the fiber resulting from storage was proposed through discussions with some of the Institute staff (100,101). Studies have been completed at the Institute on the effect of aging on pulp stored in the wet lap form, the form of storage in the present study (39-42). These studies showed that certain physical properties of handsheets from aged pulp changed as much as 10-15% compared with unaged samples. Properties affected included bonding strength, burst, tensile, tear, scattering coefficient, and pulp freeness. It was hypothesized that the changes were a result of the fibrils and fines of the pulp becoming irreversibly bonded to the fibers, resulting in pulp property changes.

Since the test fibers of this program were stored over extended periods of time, a study was conducted to determine the effects of aging on the degree of fiber cluster formation as seen by the fiber optics light probe. The fibers were stored at 40°F for a period of several months, and it was hoped to simulate the aging of the fibers undergone during this type of storage by some type of accelerated fiber aging. After discussions with Institute staff (100,101), it was decided that aging conditions could be simulated in two different ways. It was felt that treating two fiber samples, one at room temperature for approximately one week and one at 105°C for 12 hours, would effectively age the fiber. Aged and control samples were evaluated with $LaCl_3$ at pH 7 and 585 rpm. Any aging effects present would be evident after the conditioning periods. No changes in fiber-to-fiber

interactions were observed for either type of aging condition. Details of these aging studies are presented in Appendix XV.

(8) It was desired to determine the amount of the three test polymers being adsorbed by the cellulose fibers. Thus, adsorption isotherms for the three test polymers were made under test conditions used throughout the current test program. The cationic systems were evaluated at pH 5.0, the anionic systems at pH 9.0, and the nonionic systems at pH 9.0. The polymer adsorption work is somewhat inconclusive, since a suitable method for analyzing polymer systems at the very low concentrations employed was never really found. Micro-Kjeldahl techniques were employed for the analyses with the results presented in detail in Appendix XVI.

Two important findings were obtained from the polymer adsorption work. First, it was determined that the area of fiber coverage for one molecule of the cationic polymer was approximately 1×10^6 A^2. This value is in the anticipated range of 10^4 to 10^6 A^2 (102), indicating that the hydrodynamic surface area of the fiber presented in Table II was the correct area available for polymer adsorption.

Second, while the adsorption work did show cationic polymer adsorption by the fiber, no adsorption was indicated for either the anionic or nonionic polymer. This observation is supportive of the data gained throughout this study, which indicated that anionic and nonionic polymer interactions with cellulose fibers were of less consequence than the cationic-fiber interactions. It is felt that there is sufficient support in this study to conclude that the anionic and nonionic polymers did interact with the cellulose fibers, but the micro-Kjeldahl nitrogen analysis was not

sensitive enough to follow the polymer adsorption, especially at the very low concentrations employed.

FIBER-TO-FIBER STUDIES WITH FINES

The next several sections will be concerned with the extent of effect that fines addition had on the fiber-to-fiber interactions. Systems evaluated included all three test polymers both with and without $LaCl_3$ electrolyte at both low and high agitations for pH values of 5 and 9.

The results of the test systems employing polymer additives without $LaCl_3$ electrolyte are presented in Fig. 18-20 for the cationic, anionic, and nonionic polymers, respectively. Tabulated data for the three polymer systems are located in Appendix XVII. The results of test systems employing the $LaCl_3$ electrolyte are represented in Fig. 21-23 for the cationic, anionic, and nonionic polymers, respectively. Tabulated data for the polymer-electrolyte test systems can be found in Appendix XVIII.

Upon comparing fiber-to-fiber interactions without and with fines (Fig. 11 to 16 with Fig. 18 to 23, respectively), it is apparent that a 1.0% fines addition based on fiber weight did not alter either the additive concentration for maximum flocculation or the percentage change in flocculation. The percentage change is defined as the difference in the maximum flocculation value and the zero additive flocculation value divided by the latter value. By assuming the fines to be cylindrical in nature, with length of at least 9.25 μm and diameter of 0.2 μm, it was possible to calculate the surface area of the fines on a mass basis, and to compare the obtained area to the experimentally determined surface area of the fibers. A cellulose density of 1.50 g/cm^3 was used in the calculation. It was

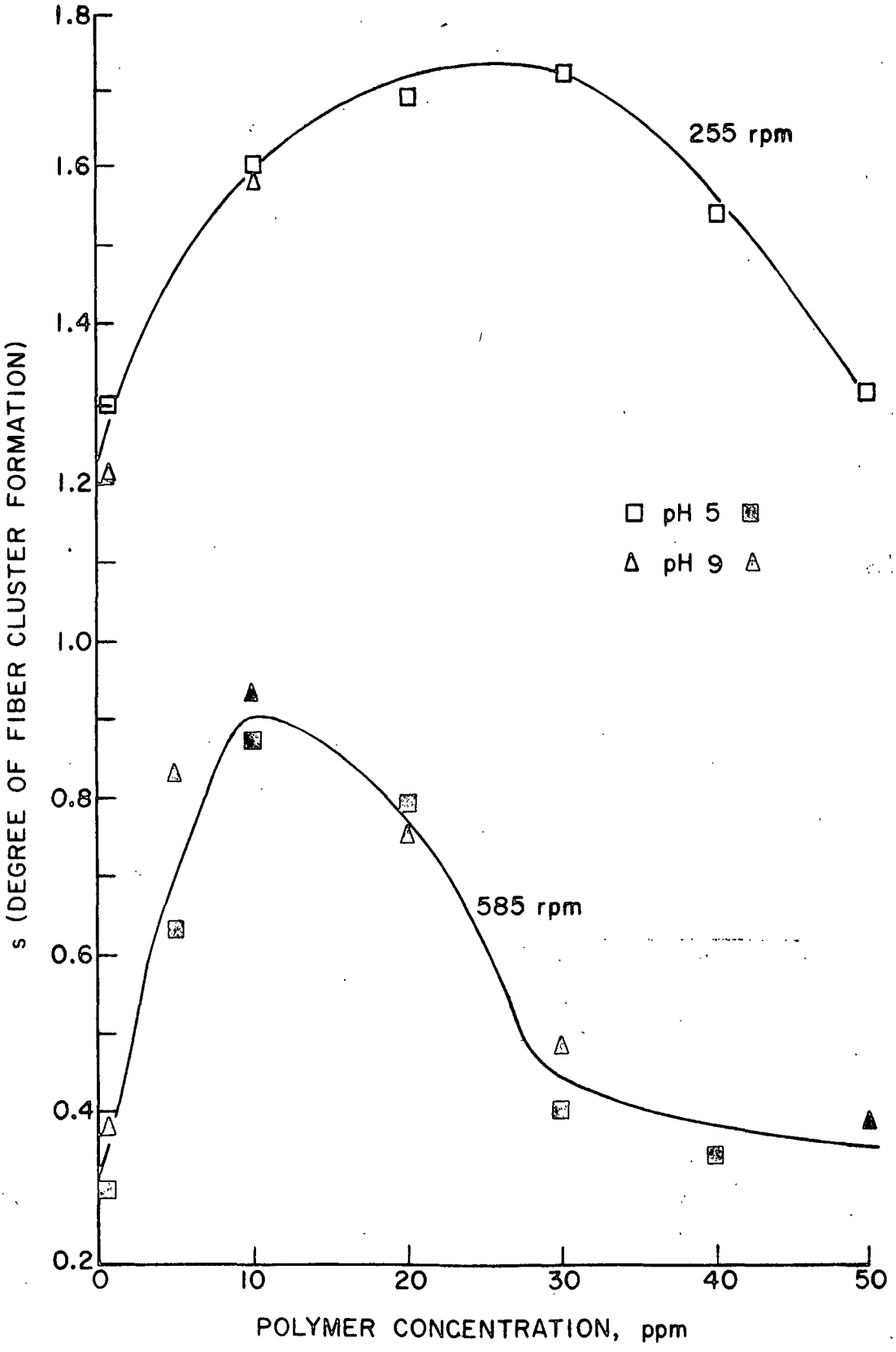


Figure 18. Cellulose Fiber Interactions as a Function of Cationic Polymer Concentration, Fines Addition, System pH, and Impeller Speed

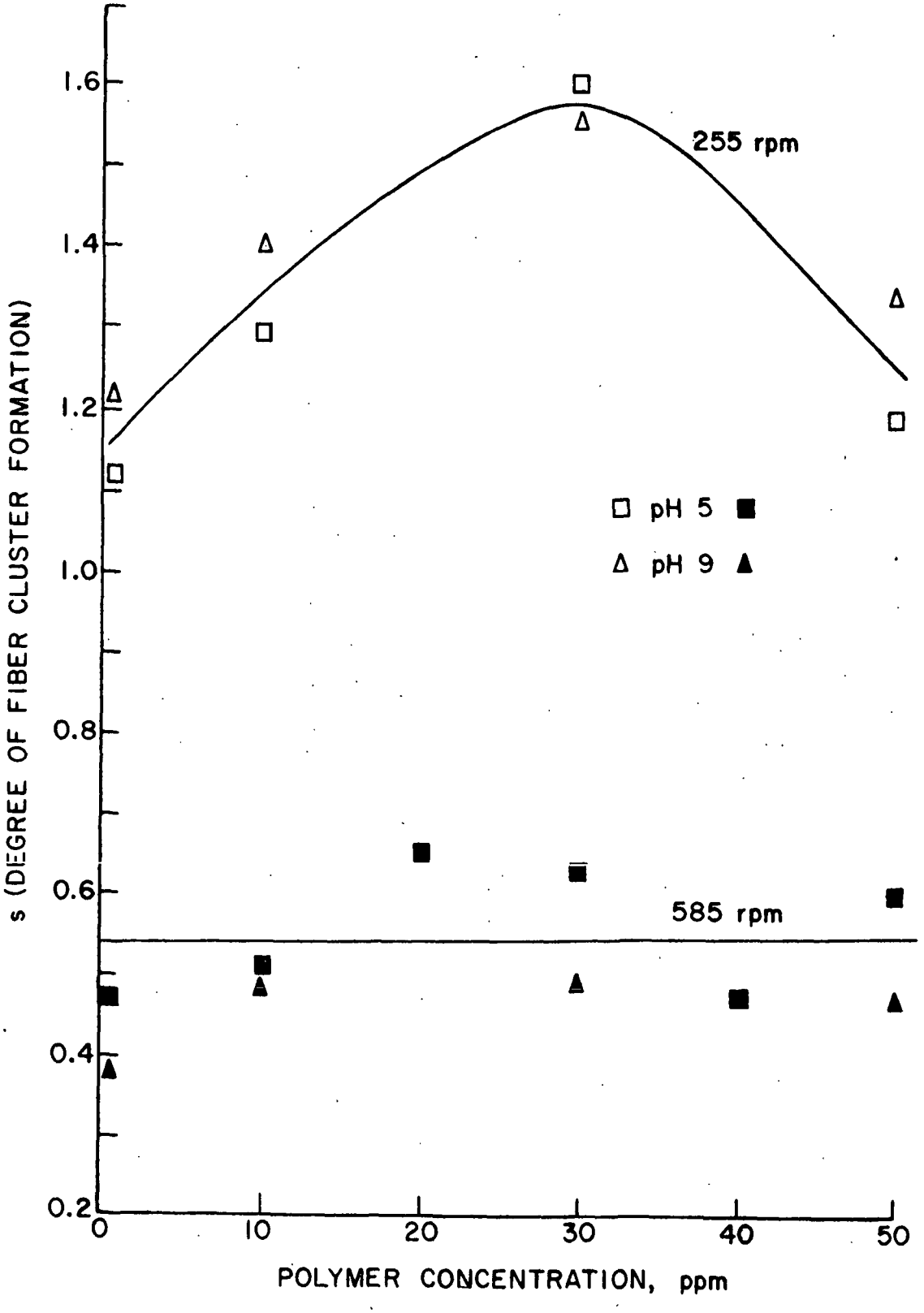


Figure 19. Cellulose Fiber Interactions as a Function of Anionic Polymer Concentration, Fines Addition, System pH, and Impeller Speed

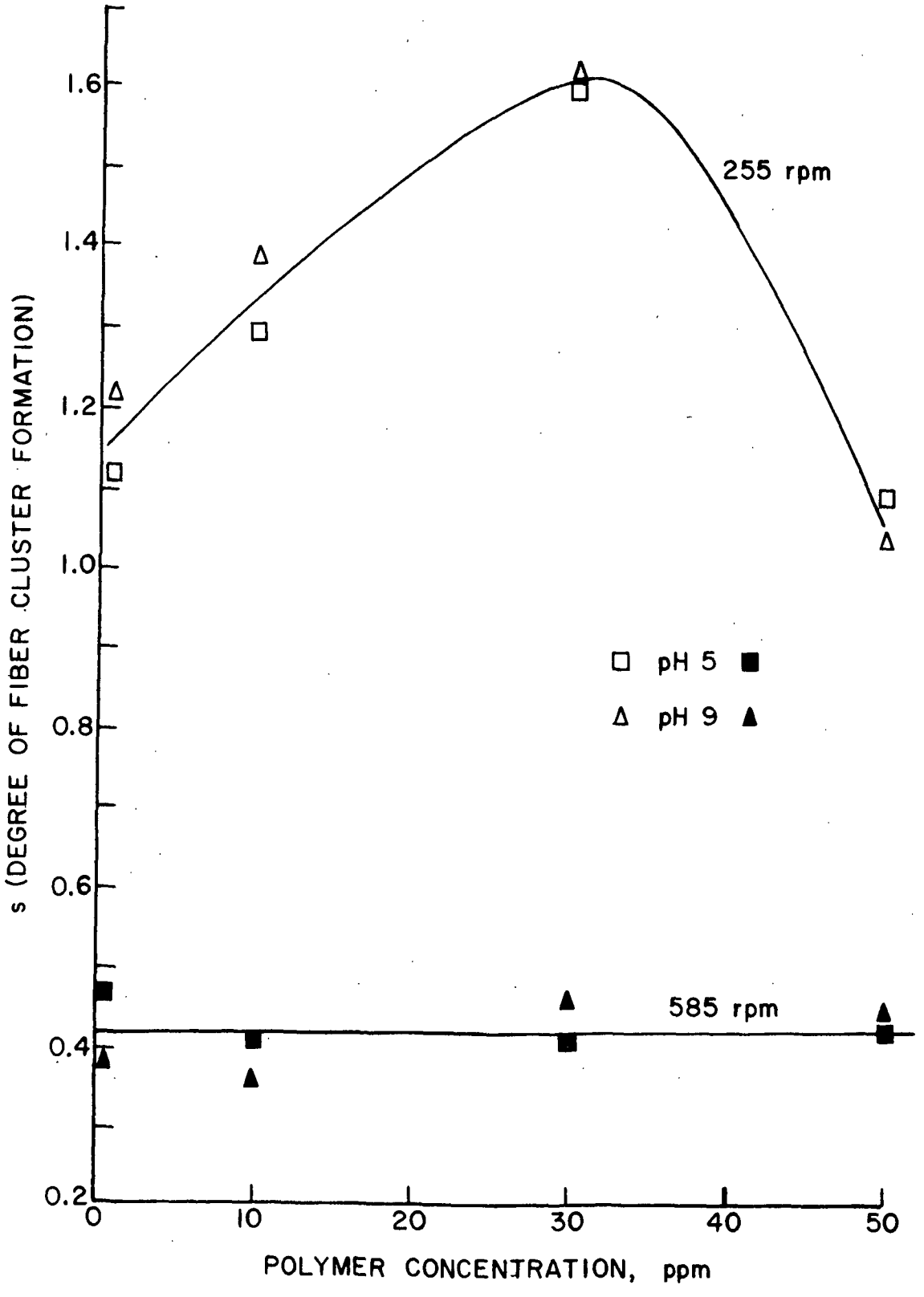


Figure 20. Cellulose Fiber Interactions as a Function of Nonionic Polymer Concentration, Fines Addition, System pH, and Impeller Speed

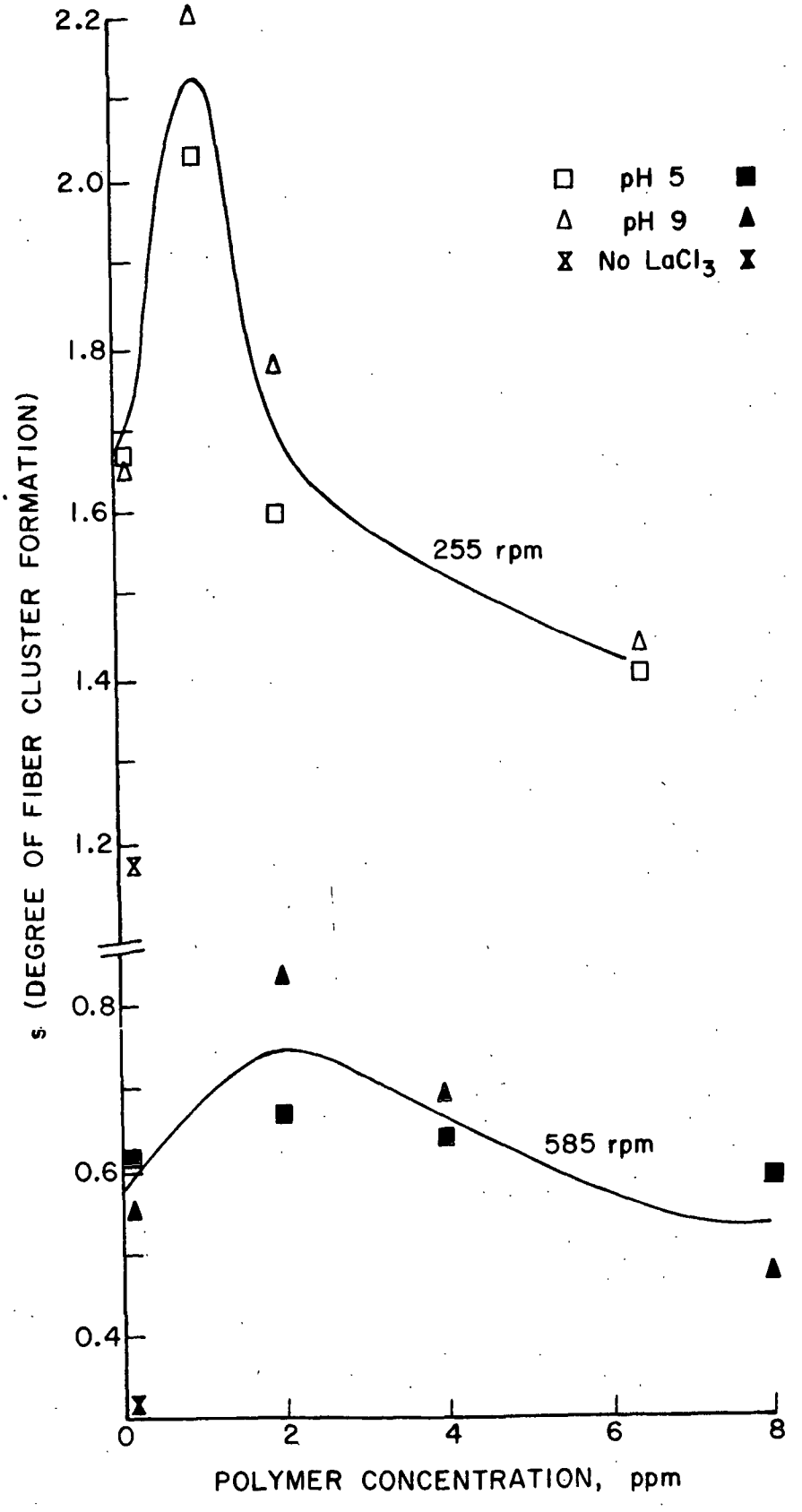


Figure 21. Cellulose Fiber Interactions as a Function of Cationic Polymer Concentration, $LaCl_3$ Electrolyte, Fines Addition, System pH, and Impeller Speed

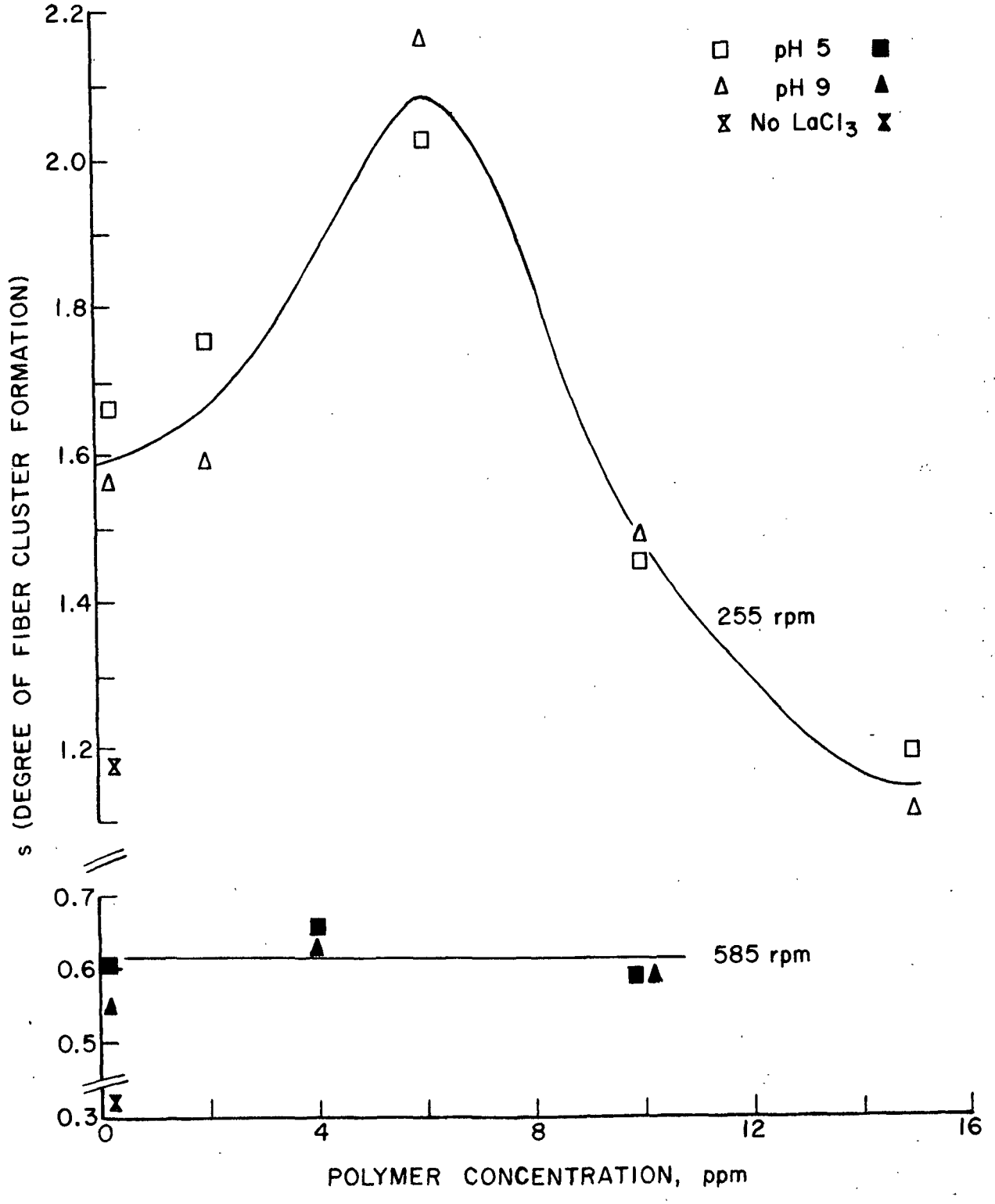


Figure 22. Cellulose Fiber Interactions as a Function of Anionic Polymer Concentration, $LaCl_3$ Electrolyte, Fines Addition, System pH, and Impeller Speed

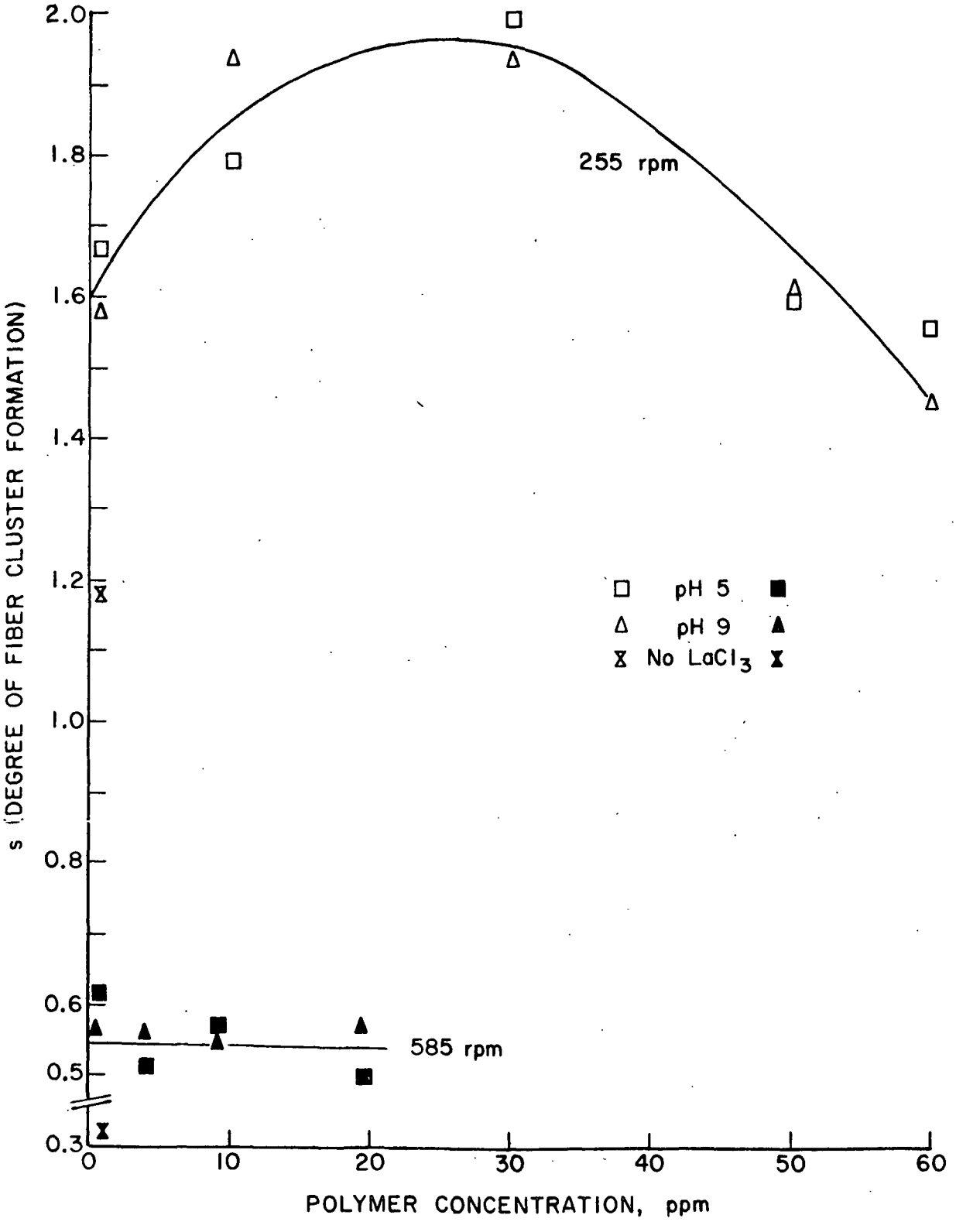


Figure 23. Cellulose Fiber Interactions as a Function of Nonionic Polymer Concentration, $LaCl_3$ Electrolyte, Fines Addition, System pH, and Impeller Speed

calculated that the surface area of the fines added to the test slurry was at least twice that of the fiber in the test slurry on a per unit gram basis. Therefore, at 1.0% fines addition based on fiber weight, there was 50,000 cm^2 per liter of furnish of total surface area available to the fiber, with an additional 1,000 cm^2 per liter of furnish of surface area associated with the fines. It is concluded that the polymers involved in this program were sufficiently active flocculating agents to maintain system flocculation even with the addition of approximately 2.0% more area in the form of cellulose fines. The polymer adsorption work discussed previously and in Appendix XVI indicated that at least 80% of the added polymer remained in solution after equilibrium with the fibers, leaving an adequate supply of polymer for the added surface area associated with the added fines.

After observing that the 1.0% fines addition did not affect fiber-to-fiber interactions, a study of 10% fines addition was conducted for the cationic polymer without $LaCl_3$ at high agitation and pH 5.0. Polymer concentrations of 0, 10, and 20 ppm were evaluated. The values of the degrees of fiber flocculation were much larger than those observed in previous fiber-to-fiber systems. Zero polymer added resulted in a degree of fiber flocculation of approximately 0.45. At the 10 and 20 ppm levels the degrees of fiber flocculation were 3.29 and 2.58, respectively. However, the maximum flocculation was still located at 10 ppm polymer with lesser values at no polymer and 20 polymer.

The polymer flocculation value at zero concentration is an estimated value, because the 100 data points were mistakenly collected at 255 rpm instead of 585 rpm. The 255 rpm value of 1.07 was in complete agreement

with all previous studies, and so it was felt that it was justifiable to supply an average value for the 585 no-polymer flocculation value.

It is apparent from this study coupled with the 1.0% fines work, that the fines do play a role in the fiber-to-fiber interactions as seen by the fiber optics light probe. Also, it is concluded that the concentration of the fines was a critical factor, with the 1.0% coverage having no influence on fiber interactions, while the 10% fines coverage greatly affected fiber interactions.

There is no concrete explanation for the observed effects, but a little speculation may be useful. One possible explanation is that the fines are flocculated to such an extent that they become large aggregates, appearing as fiber clusters to the light probe. However, this possibility is not likely, since the fines are such small particles to begin with. It is probable that the fines particles extended the bridging power of the polymers by forming networks of fiber-fines-polymer agglomerates. The network could be visualized as a three-dimensional arrangement of -[-fiber-polymer-fine-polymer-fiber-polymer-]$_n$- as a type of repeating unit where, without the significant fines level, the repeating unit would be predominately fiber-polymer-fiber. Since the building units of the network with increased fines level would be larger and more extensive than without fines, the entrapment and entanglement ability of the network would be increased. The two influences of enlarged building units plus increased entanglement could result in the large degree of flocculation seen by the fiber optics light probe.

All experimental data points as obtained from the photographic film for the fiber-to-fiber interactions have been stored on computer tape. This computer tape plus a printout of the data has been filed with Professor Dale G. Williams, current thesis chairman, if needed for future reference.

FINES-TO-FIBER STUDIES

The discussion will now turn to the carbon-14 radioactively tagged fines-to-fiber interactions, with all three test polymers evaluated. Fines retention was checked with and without $LaCl_3$ electrolyte at both agitation conditions for pH values of 5 and 9.

POLYMER STUDIES WITHOUT ELECTROLYTE

The first series of results to be considered is concerned with the effects of the three test polymers without electrolyte on fines retention. The results of the cationic, anionic, and nonionic polymers are presented in Fig. 24-26, respectively. Tabulated experimental data for these three figures can be found in Appendix XX.

The first point of importance is that the curve shapes for systems showing increased fines retention were completely different from the fiber-to-fiber systems. Cationic-low agitation, cationic-high agitation, anionic-low agitation, and nonionic-low agitation indicated increases in fines retention through certain polymer concentrations, but did not show redispersive tendencies at the higher polymer concentrations. For example, the cationic polymer was carried out to 120 ppm concentration without a reduction in fines retention. At these high polymer concentrations, redispersive tendencies were very pronounced for the fiber-to-fiber test systems.

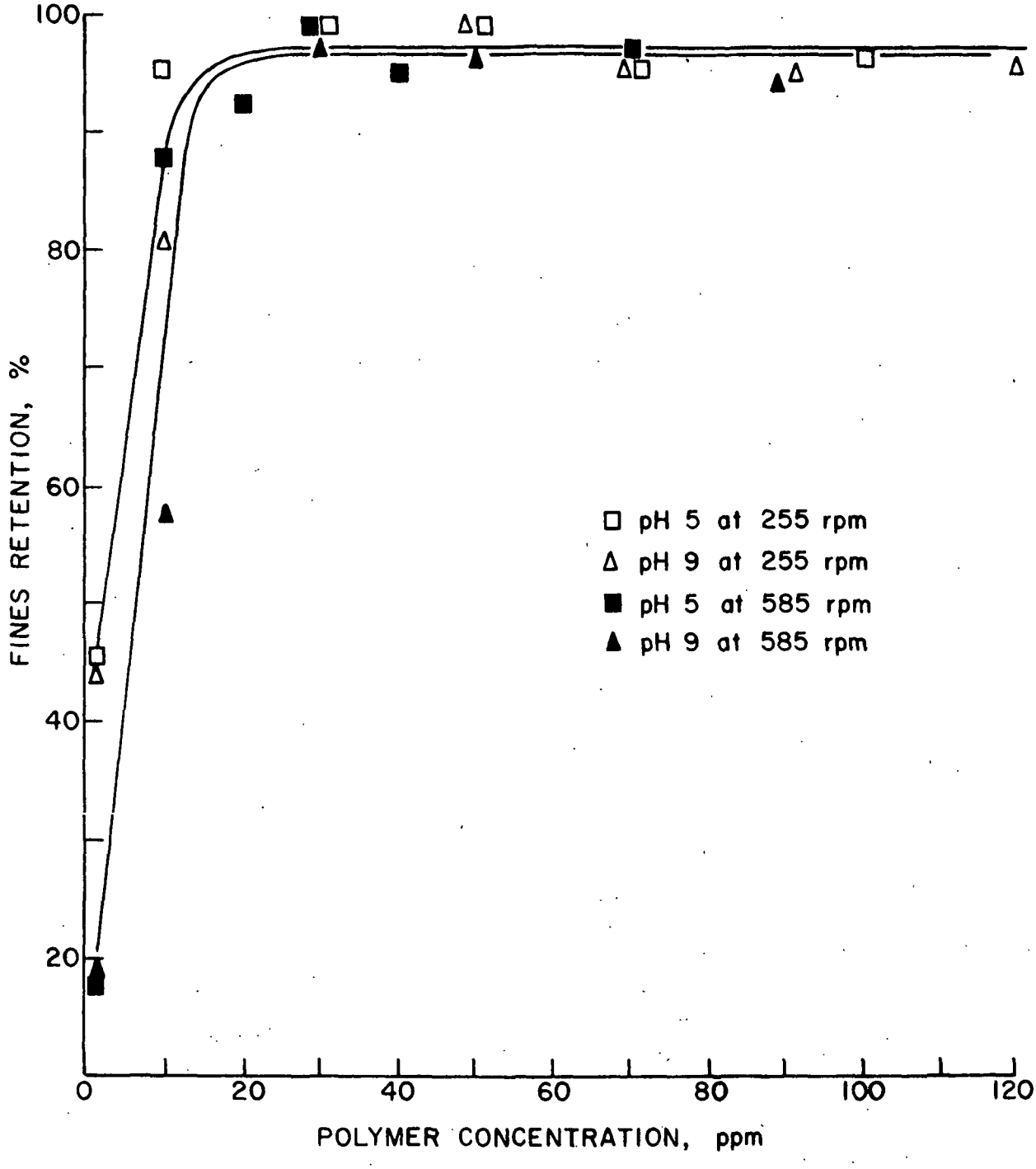


Figure 24. Cellulose Fines-to-Fiber Flocculation as a Function of Cationic Polymer Concentration, System pH, and Impeller Speed

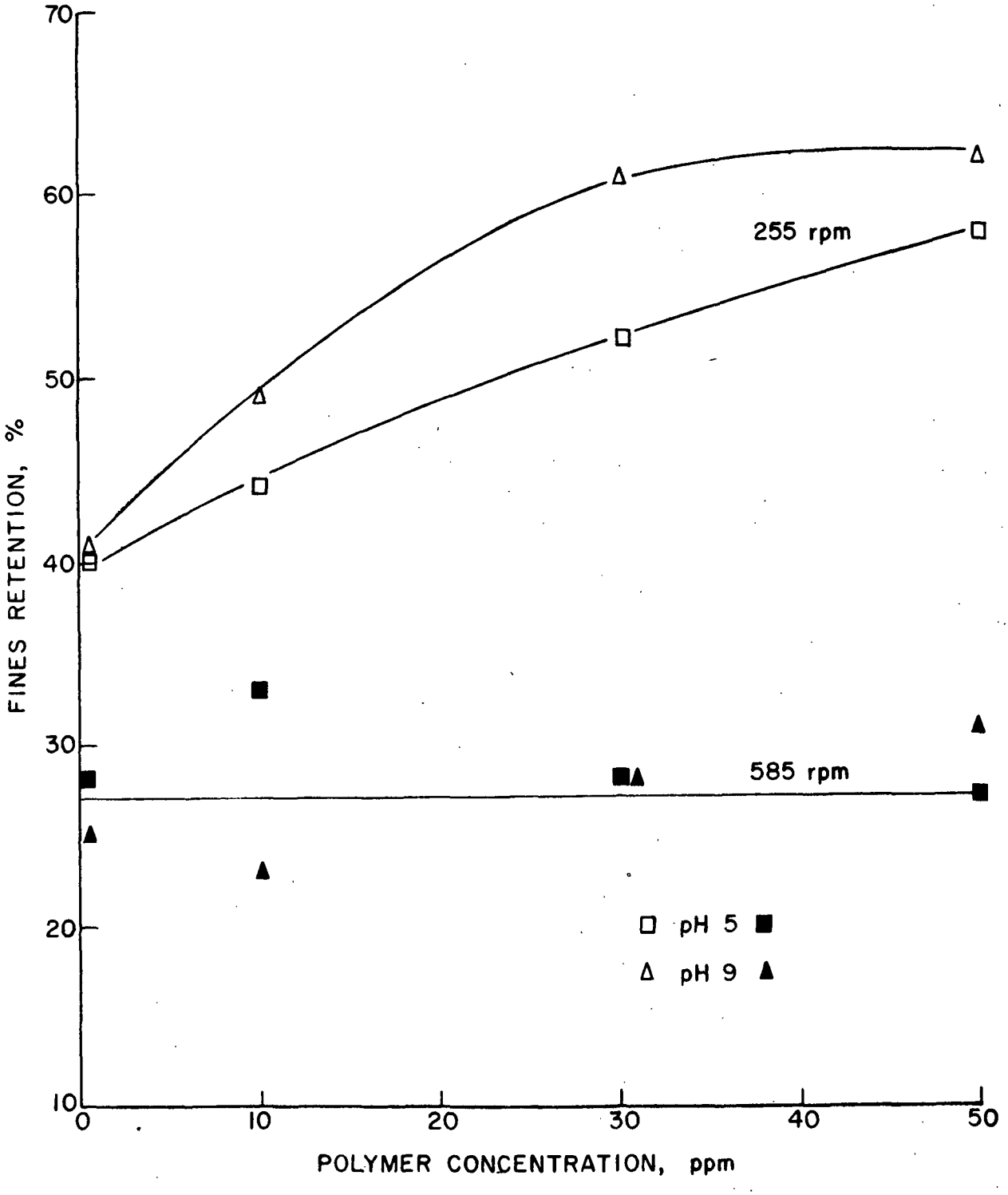


Figure 25. Cellulose Fines-to-Fiber Flocculation as a Function of Anionic Polymer Concentration, System pH, and Impeller Speed

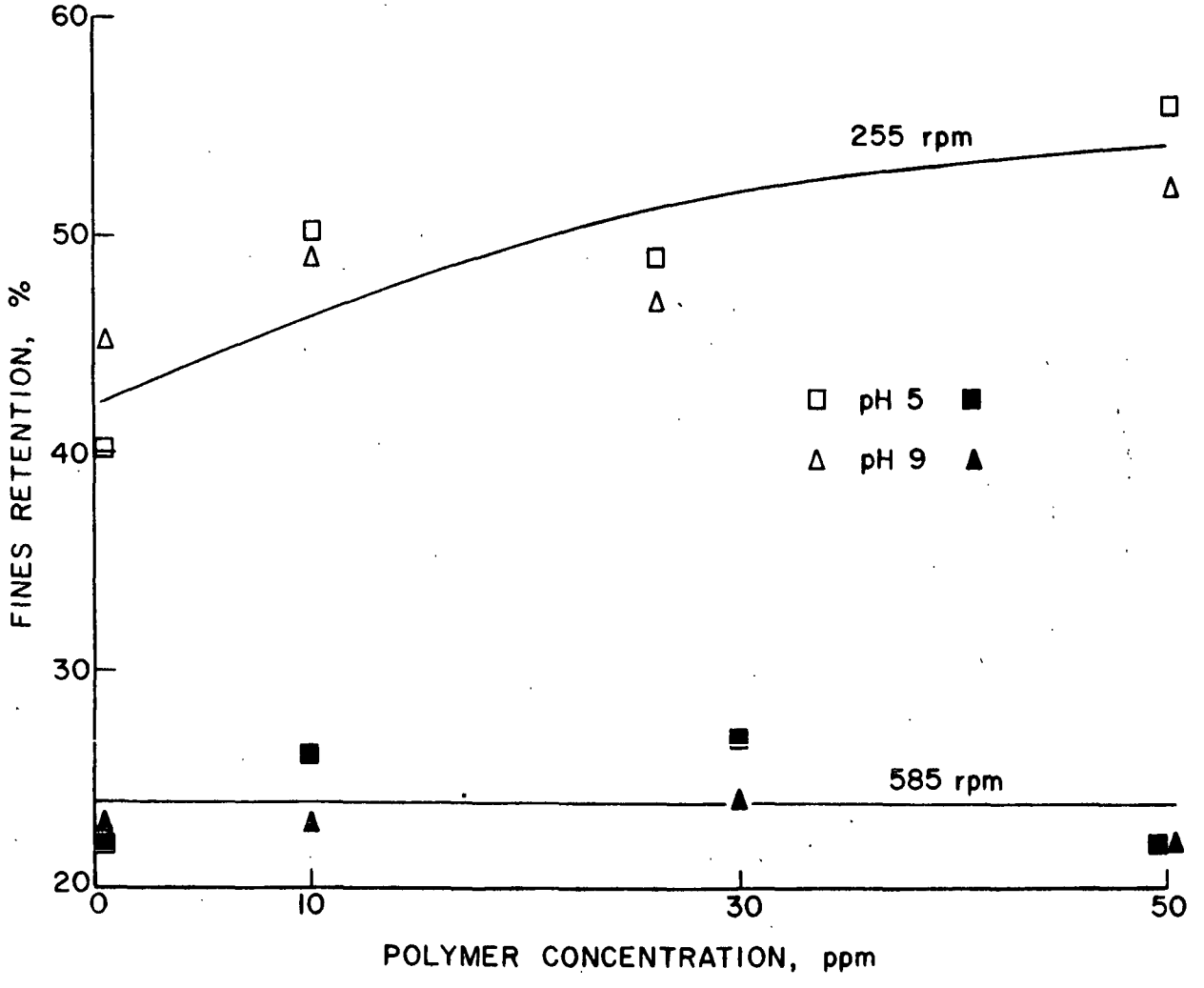


Figure 26. Cellulose Fines-to-Fiber Flocculation as a Function of Nonionic Polymer Concentration, System pH, and Impeller Speed

It would be anticipated that, similarly to the cellulose fibers, the cellulose fines would be redispersed at some polymer concentration. This redispersive polymer concentration would be reached when either sufficient charge was built up on the fines surface, or the polymer completely covered the particle resulting in a redispersive effect via a protective entropy barrier. However, redispersion of the fines was not reached over the polymer concentrations studied.

According to the polymer bridging model proposed by LaMer and Smellie (70), the rate of disintegration of spherical particles is directly proportional to the weight of the particle and inversely proportional to the surface area of the particle. The weight of the particle represents a factor tending to pull the network apart, while the surface area retards the decrease in network size by particle binding through increased polymer adsorption. Although the cellulose materials are not spherical, the comparison of fiber weight and surface area to fines weight and surface area can be made. The smaller weight of the fines coupled with their larger surface area than the fibers indicates that the polymers would have a stronger flocculating influence on the fines than on the fibers at the same agitation. This is in fact what has been shown in the current study, since the fines were retained over a much larger polymer concentration range than were the fibers flocculated. This observation along with the previous observation that the fiber-to-fiber and fines-to-fiber systems behaved similarly under the influence of electrolyte-only, supports the idea that polymer bridging is perhaps more important in the current test systems than is charge reversal.

There was a dependence on pH for some of the fines retention systems, but only at concentrations where the fines retention was not yet complete. For the cationic system at low agitation, there was a 14% greater fines retention at 10 ppm polymer for pH 5 than found at pH 9. Similarly, at high agitation and 10 ppm cationic polymer, there was a 30% increase for pH 5 over pH 9. On the other hand, the anionic polymer at low agitation indicated that pH 9 systems gave 6 to 7% better retention than did pH 5 over the entire concentration range. The nonionic polymer system was not pH dependent at either the low or high agitation condition. The fact that pH dependence was demonstrated for the polymer fines systems and not for the polymer-fiber systems is notable, indicating that the pH effects were perhaps present for the fiber systems, but not seen by the light probe.

There are two possible explanations for the observed pH effects. First, the changes associated with the cellulose surface charge on pH change may alter the degree of polymer adsorption to the cellulose. For the cationic polymer, pH 5 would result in a less negative character for the cellulose surface, while pH 9 would lead to a more negative surface. For pH 5, the hydrogen ion probably acts to suppress the ionization of carboxylic acid groups of the hemicelluloses and phenolic hydroxyl groups of lignin. By decreasing the negative character of cellulose at lower pH values, it would be expected that the cationic polymer would be a less effective adsorber, and so a less effective flocculant. But, the cationic polymer is more effective at pH 5 than at pH 9, so that an alternate explanation is required.

Second, changes in pH may affect the extent to which the polymer interacts with the cellulose particles by altering the polymer charge characteristics. This change in interaction may be accomplished in two ways: by

increased or decreased electrostatic interactions and by the coiling or uncoiling of the polymer chains. The tertiary amine group of the cationic polymer picks up protons from solution, and so the lower the pH value the more polymer functional groups that acquire a positive charge. This more positive character of the polymer at lower pH values would increase the polymer-cellulose interactions making the polymer a better flocculant. This increased charge can also result in increased uncoiling of the polymer chains, via electrostatic repulsion (103). As the polymer chains become longer and less entangled with each other, the polymer becomes a better flocculant.

It is clear that the observed pH effects are in the opposite direction than would be required for an explanation of cellulose structure changes. However, the pH effects can be explained by the influences that pH changes would have on the charge characteristics of the polymer molecules. The fact that the nonionic polymer was not influenced by pH changes is one more piece of evidence supporting polymer charge effects and not cellulose charge effects.

Higher pH would result in more negative character in the carboxylic acid functional sites of the anionic polymer, resulting in an increased uncoiling of the polymer chains. The increased uncoiling of the polymer at elevated pH would result in longer polymer chains and thus increased flocculating ability (103). The anionic polymer-cellulose interactions were probably a result of hydrogen bonding of the polymer amide groups and cellulose carboxyl groups.

It does appear that, if the pH results for fines retention were explained on the basis of polymer chain expansion, then the increased flocculation power would influence fiber-to-fiber systems to the same degree as the fines-to-fiber systems. Either the agitation forces for the fiber-to-fiber systems were sufficient to negate the pH effect, or the fiber optics light probe was not sensitive enough to follow the fairly small pH effect.

Finally, note that the agitation results for the fines-to-fiber and fiber-to-fiber interactions were generally the same, with cationic polymer showing fiber flocculation and fines retention at both 585 and 255 rpm, while the anionic and nonionic polymers did not exhibit any influence at 585 rpm. This result is somewhat surprising, since it was anticipated that the flocculation of the more massive and longer fibers would be more dependent on the turbulence of the slurry than would be the smaller fines particles.

It can be concluded from this study, that it is indeed possible for a fiber slurry to be well dispersed leading to good sheet formation, while at the same time having good cellulosic material retention. It is important to note that this study has demonstrated the possibility of the above combination of events, but has not said that in mill situations the correct set of conditions will be obtainable.

POLYMER STUDIES WITH ELECTROLYTE

Systems evaluated in this section include the three test polymers at both low and high agitation for pH values of 5 and 9. All test systems contained a 1×10^{-4} M background concentration of $LaCl_3$ electrolyte. The results of these evaluations are presented in Fig. 27-29 with tabulated

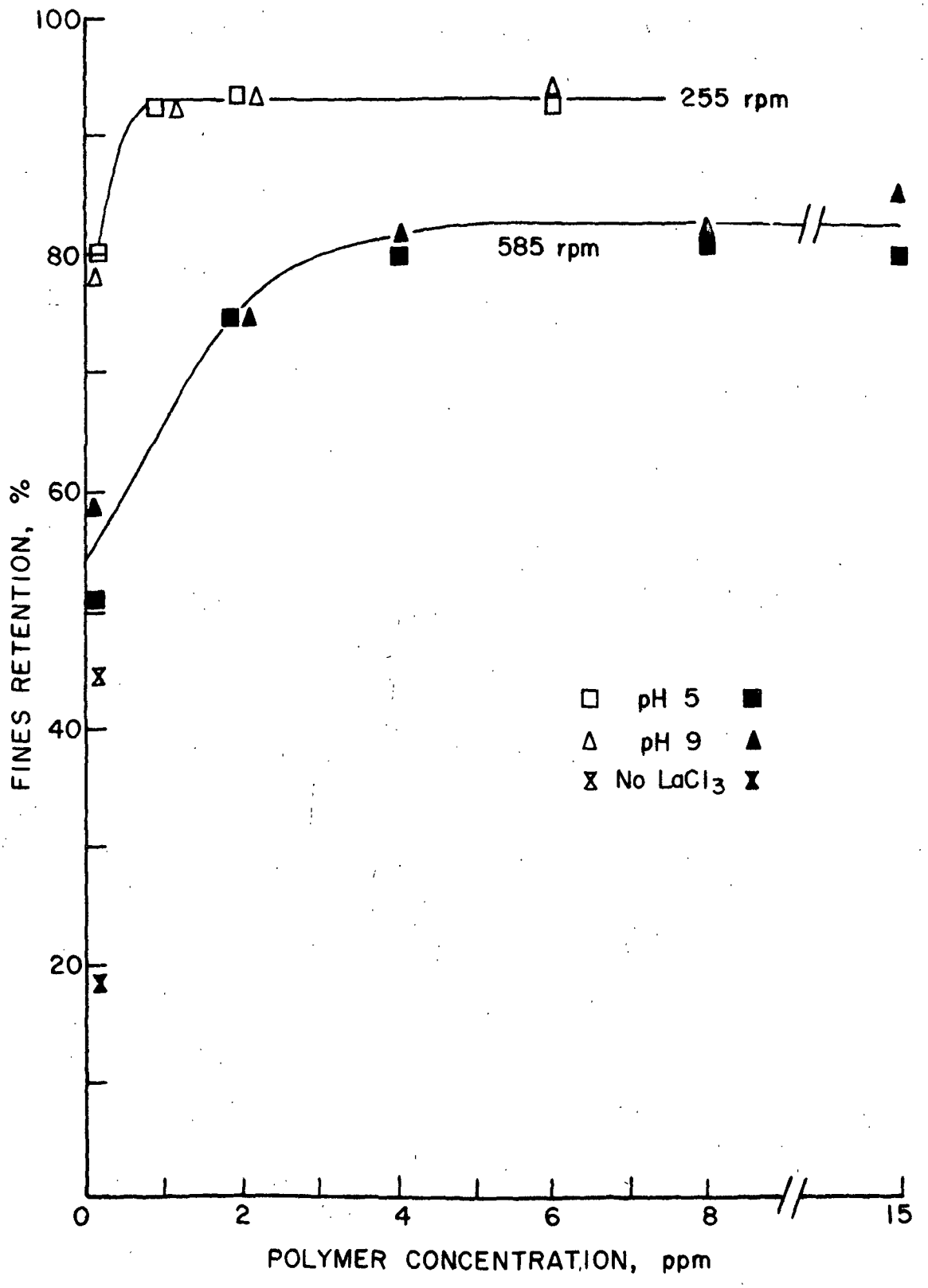


Figure 27. Cellulose Fines-to-Fiber Interactions as a Function of Cationic Polymer Concentration, $LaCl_3$ Electrolyte, System pH, and Impeller Speed

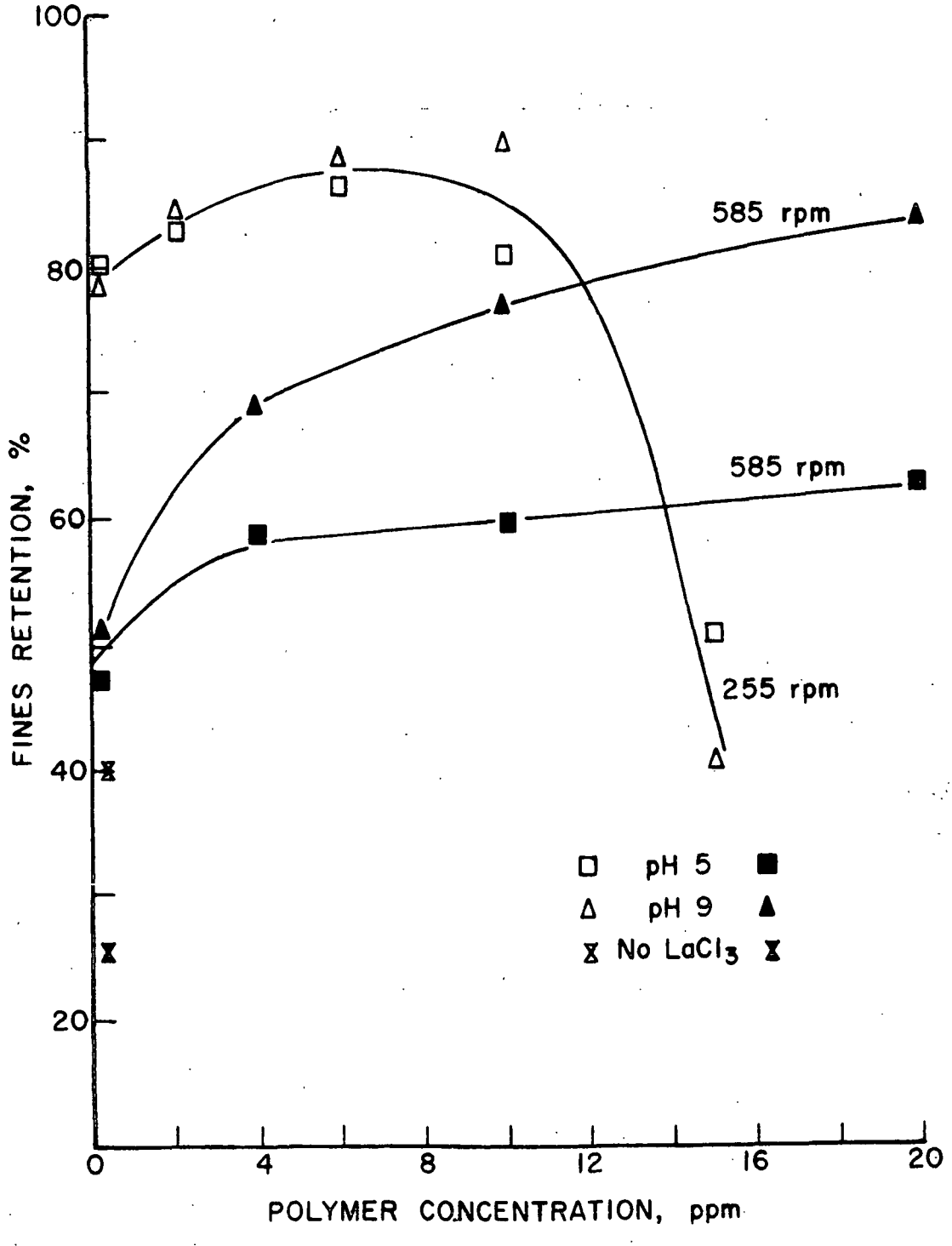


Figure 28. Cellulose Fines-to-Fiber Interactions as a Function of Anionic Polymer Concentration, $LaCl_3$ Electrolyte, System pH, and Impeller Speed

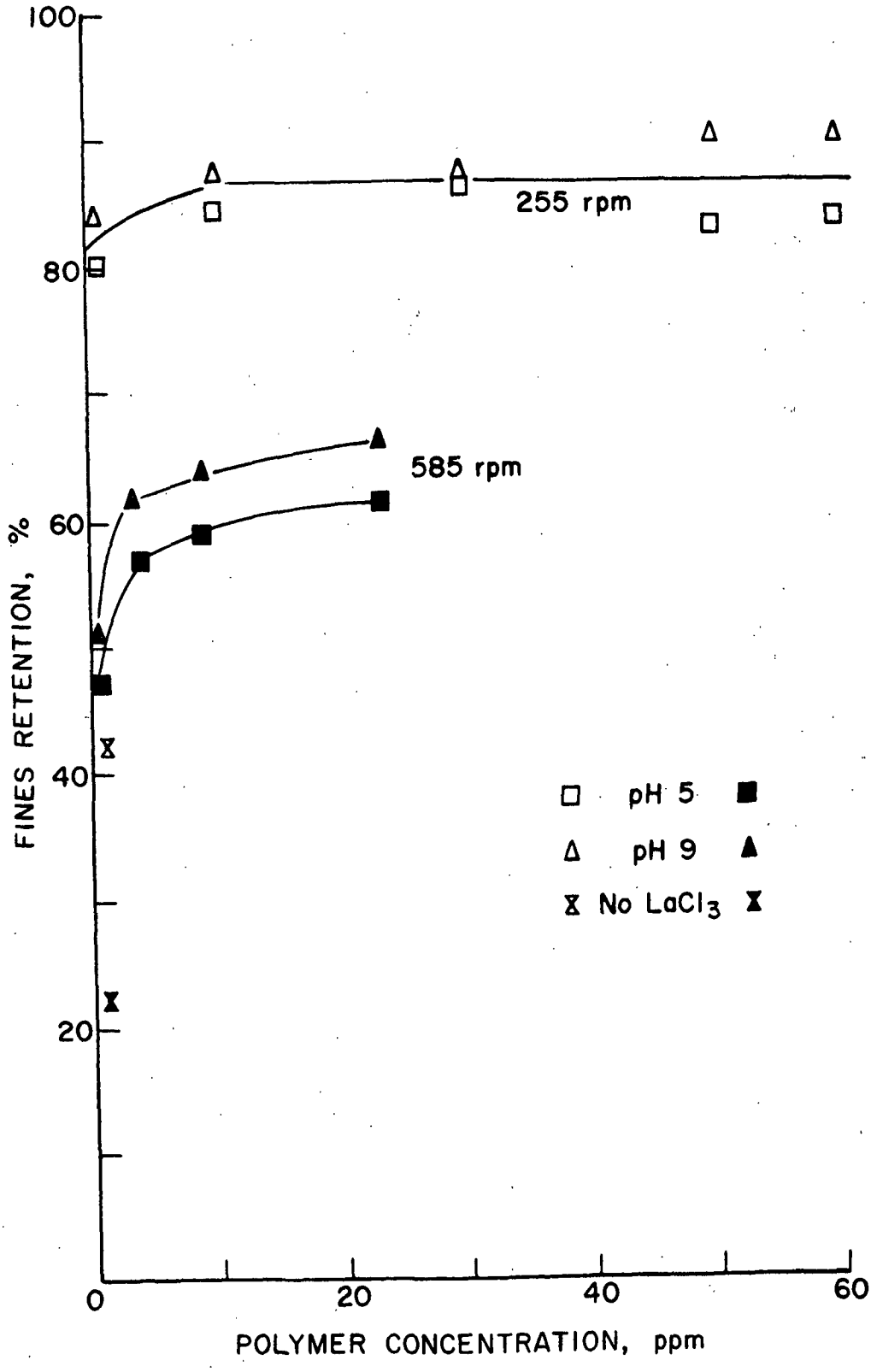


Figure 29. Cellulose Fines-to-Fiber Interactions as a Function of Nonionic Polymer Concentration, $LaCl_3$ Electrolyte, System pH, and Impeller Speed

data located in Appendix XX. The results obtained here were somewhat surprising, considering the results obtained for the fines retention studies without $LaCl_3$.

The cationic system behaved differently with the $LaCl_3$ electrolyte than without electrolyte for the fines retention studies. Notable differences included lower levels of retention with $LaCl_3$, and less retention at 585 rpm than at 255 rpm when $LaCl_3$ was used. Similarly, the anionic system had major differences with $LaCl_3$ including: a distinct fines retention at elevated agitation, and a strong redispersive tendency at low agitation. The nonionic polymer did show a pH dependence with $LaCl_3$ where there had not been without $LaCl_3$. Also, the nonionic polymer showed a larger increase in fines retention at 585 rpm than at 255 rpm with the addition of $LaCl_3$.

The addition of $LaCl_3$ has the following effects on the cellulose and charged polymers. The double layer of the cellulose is compressed and/or collapsed, resulting in the cellulose particles being able to approach each other more closely without electrostatic repulsion. Upon $LaCl_3$ addition, the coiled structure of the polymer is collapsed and made smaller by much the same mechanism as when an electrolyte collapses an electric double layer (102,103). The result of the polymer collapse is that the polymer chains taking part in bridging are shortened. The shortened chains are less effective in bridging particles together, thus the polymer flocculating power is reduced. The electrolyte addition has significantly altered the double layer influence as seen by the increases of fines retention in Fig. 27-29 for electrolyte only. The collapsing of polymer molecule chains results in the poorer flocculating ability of the affected polymers. This effect is seen in the lowering of maximum fines retention for the cationic polymer, while being notably absent for the anionic and nonionic polymers.

Test results indicated that the $LaCl_3$ addition weakened the cationic polymer as a flocculating agent, while improving the flocculating power at both the anionic and nonionic polymers. The fines retention for the cationic system at 585 rpm is lower with $LaCl_3$ than without $LaCl_3$ (Fig. 24 and 27). The anionic system with $LaCl_3$ resulted in much improved retention over no $LaCl_3$ at both 255 and 585 rpm (Fig. 25 and 28), while the nonionic system showed similar results as did the anionic polymer (Fig. 26 and 29).

It is possible that the La(+3) was competing with the positive cationic polymer for adsorption sites on the cellulose. This competition for adsorption sites along with the collapsing of the polymer structure was sufficient to render the cationic polymer a less effective flocculant with $LaCl_3$ than without the electrolyte.

On the other hand, the $LaCl_3$ collapsed the cellulose double layer permitting the particles to approach each other more closely. Thus, the anionic and nonionic polymers were able to interact with the cellulose more effectively, even though the polymer chains were shortened by the $LaCl_3$. Once again the anionic and nonionic interactions with cellulose were probably a result of hydrogen bonding.

The redispersion of test fines by the anionic polymer at low agitation and not at high agitation is another observation difficult to explain. It is not likely a charge reversal effect since an electrostatic effect would be effective at both low and high agitation. At this time, the author has not been able to explain the observed redispersion by the anionic polymer at low shear.

In explaining the pH effect found for the nonionic polymer, it is important to note the possibility that a certain amount of hydrolysis can take place during the commercial production of the polymer. Thus, there is the possibility that the nonionic polymer contains a small number of carboxylic acid functional groups. These acid groups would be more completely ionized at pH 9 compared to pH 5, thus explaining the improved fines retention for the nonionic polymer at pH 9 and 585 rpm.

In general, fines-to-fiber interactions with $LaCl_3$ were maintained over broader polymer concentration ranges than were the fiber-to-fiber interaction under similar test conditions. Considering the extent of electrolyte backgrounds found in most mill situations, generally in the form of Al(+3) instead of La(+3), along with the results of this study, it still remains possible that fiber-to-fiber interactions could be reduced while still maintaining good fines retention in the finished product. If the optimum conditions can be reached in the mill, then better sheet formation could be obtained while maintaining good cellulose material retention.

SUPPORTIVE STUDIES

Systems which were required as supportive evidence for the fines-to-fiber interactions included a study on the influence of extended periods of agitation on system interactions, a study on the effect of increased fines additives on system interactions, and a study to determine the amount of fibers passing through the fines sampling port. This system of the paper is concluded with a discussion on the spread in the data of the three separate countings of the carbon-14 samples.

(1) Time of agitation studies were conducted on all three test polymers both with and without $LaCl_3$, at 585 rpm only. Only 585 rpm was used, since it was assumed that if no dependency on agitation was seen at 585, then it probably would not show up at 255 rpm. The test evaluations without $LaCl_3$ were conducted at pH 7.0. The cationic evaluations with $LaCl_3$ were conducted at pH 5.0, while the anionic and nonionic evaluations with $LaCl_3$ were conducted at pH 9.0. The results of these agitation studies are presented in Appendix XXI. The results of this test indicated that extended periods of agitation at 585 rpm did not cause any loss of fines retention. This observation is in agreement with the time of agitation studies on fiber-to-fiber interactions, which also did not show an effect on extended agitation. Both of these system results are in disagreement with Chiu (43) and Muhonen (69), both of whom observed a decrease in fiber flocculation and Chiu only in fines retention on extended agitation periods for an alum-polyelectrolyte system. The present polymer system is apparently a strong enough bonding agent to the cellulose, that the prolonged agitation does not destroy polymer bridges.

(2) At the same time that the fiber-to-fiber interactions were evaluated at a 10% fines addition level, the fines-to-fiber interactions were also monitored. No differences in fines-to-fiber interactions for the 10% system were observed as compared to the 1% system. The retention values obtained for no polymer, 10 ppm cationic polymer, and 20 ppm cationic polymer were 11.7, 86.3, and 96.0%, respectively. The system was evaluated at 585 rpm and pH 5. The increased fines coverage had no effect on the percentage of fines retained at the same polymer addition levels.

By comparing the fiber and fines surface areas along with polymer addition and retention levels, it was found that there was adequate polymer for both the fiber and fines present. As stated previously, the fines surface area was assumed to be approximately twice as great as the fiber surface area on a per gram basis. Based on the polymer adsorption work (20% of added polymer went to the fiber at monolayer coverage) plus a polymer addition level of 0.004-g polymer per g fiber, it was calculated that 1.6×10^{-4}-g polymer was required to form monolayer coverage of the added fines. There was 8.0×10^{-4} g of polymer required to form monolayer coverage of the fibers present, for a total polymer consumption of approximately 1×10^{-3} g of polymer. There was added to the slurry 4×10^{-3} g of polymer, so that approximately 25% of the added polymer was adsorbed by the cellulose materials.

It is important to note that the fines retained at 10% addition levels reached a maximum retention value at 20 ppm polymer, while the fibers were in the redispersion region by this concentration. Thus, it still remains possible to achieve fiber dispersion, while maintaining good fines retention.

(3) Another matter of importance was the amount of fibers which passed through the sampling screen, bringing fines attached to them into the sample vials. If a significant number of fibers were passing through the screen, then the retention would appear to be lower than it actually was. Therefore, fibers were placed in the tank at 0.5% consistency and agitated at 585 rpm. Samples of the supernatant were collected through the sample port, oven dried, and weighed to determine the weight of fiber passing through the screen. The results of this study are presented in Table IV.

TABLE IV

DETERMINATION OF FIBER WEIGHT ENTERING SAMPLE PORT

Trial	Tare	Slurry + Tare, wet	Slurry, ml	Fiber + Tare, dry	Fiber, dry	Fiber/ml, g	Average Fiber/ml
1	17.1106	32.5888	15.4782	17.1109	0.0003	1.94×10^{-5}	2.26×10^{-5}
2	17.2167	32.7272	15.5105	17.2171	0.0004	2.58×10^{-5}	

The amount of fiber coming into the sample port was 2.26×10^{-5} g/ml, which is 0.001% of the total fiber present in the tank. There were 940,334 counts per minute in the entire slurry, and if complete retention is assumed, then only 9.4 counts per minute would come through the sampling screen via the retention of the fines by the fibers. This 9.4 cpm is of the order of the water background counts.

(4) A typical set of data for three carbon-14 counted samples gave counts per minute of 1124.44, 1190.38, and 1105.46. The average of these three values was 1140.09 ± 44.57 for an average percentage deviation of ±3.9%. All of the experimental data obtained from the liquid scintillation counter for the carbon-14 fines retention studies have been stored on computer cards. These cards plus a printout have been filed with Professor Dale G. Williams for future reference.

COMPARISON OF TEST SYSTEMS

In this section the test results will be reviewed in a comparison of the three test systems: (1) fiber-to-fiber with fines, (2) fiber-to-fiber without fines, and (3) fines-to-fibers.

Fiber-to-fiber interactions with and without fines did respond differently under the influence of polyelectrolyte retention aids. Although there was a maximum in flocculation with redispersion at higher polymer concentrations for both systems, the degree of flocculation was much larger for the fines system than without the fines. However, the change in flocculation was dependent on the amount of fines present, since a 1.0% fines addition level caused no changes in the degree of fiber flocculation, while the 10% fines addition level resulted in very large fiber flocculation increases.

It is felt that the presence of the fines allowed the formation of a more extensive floc network than at low fines levels, with the fines serving as a part of the polymer bridge. This extended floc network was physically larger than at the lower fines concentration as seen by the light probe, plus it was more able to form entangled fiber networks because of the increased flexibility of the longer fiber-polymer-fines-polymer-fiber building blocks.

The fiber-to-fiber interactions and the fines-to-fiber interactions reacted similarly under the influence of simple electrolyte additives, but quite differently under the influence of polyelectrolytes. Both systems were coagulated at the same electrolyte concentration, and both remained coagulated with additional electrolyte concentration. However, concentration effects as well as curve shapes were different for the polymer only and polymer plus electrolyte systems. Under the polymer influence, the fiber systems showed maximum degrees of flocculation at a certain polymer concentration with redispersion occurring with increased polymer additions. On the other hand, the fines remained attached to the fibers well past the polymer concentrations where the fibers became dispersed.

The fact that the fines particles were retained more efficiently over broader polymer concentrations than were the fibers flocculated is in agreement with the picture of polymer bridging presented by LaMer and Smellie (70). The smaller a particle radius the less is its weight, which is a factor tending to destroy polymer bridges. At the same time, the more surface area a particle has, the better is polymer adsorption, with the result of more and stronger bridges. The fines are smaller in size than the fibers and also have more surface area than the fibers, indicating that fines-to-fiber interactions via polymer bridging should be more intense than fiber-to-fiber interactions.

Fines-to-fiber systems were shown to be dependent on pH only before complete retention was achieved, while fiber-to-fiber systems both with and without fines did not show any pH dependency. It was felt that the sensitivity of the fiber optics light probe detection method was not adequate to observe the small fluctuations in fiber-to-fiber interactions on pH changes, where the liquid scintillation counting of carbon-14 was able to detect the pH effects for the fines-to-fiber systems.

The fines-to-fiber systems exhibited a pH dependency for the charged cationic and anionic polymers, but not for the noncharged nonionic polymer. In general, the pH effects were explained on the pH dependence of the functional groups associated with the polymers. For the cationic polymer the tertiary amine groups would be more completely charged under acid conditions; thus, pH 5 was a better test condition than pH 9. For the anionic polymer the carboxylic acid groups would be more fully charged at pH 9; thus, pH 9 was a better test condition than pH 5.

Agitation effects were important for the polymer test systems, both with and without electrolyte but not for the electrolyte only systems. Changing the agitation from 255 to 585 rpm on the electrolyte fiber-to-fiber system resulted in no changes of curve shape or amount of electrolyte required to coagulate the system; except for $LaCl_3$ which did show coagulation at lower concentration at the higher agitation. The $LaCl_3$ effectively collapsed the double layer so that the increased particle collision frequency and energy resulting from increased agitation dominated the destruction forces of increased agitation. The increased collision frequency and energy resulted in more complete fiber coagulation at lower $LaCl_3$ concentrations.

On the other hand, agitation changes always affected polymer systems for both fines and fiber studies. For the fiber-to-fiber interactions with cationic polymer, less polymer was required to achieve maximum flocculation at high agitation than for low agitation. This result indicated once again that the increased collision frequency and energy parameters were more important than the disruptive forces of increased agitation. For the anionic and nonionic polymers, reduced or no cellulose-polymer interactions were found at elevated agitations indicating the inability of the anionic and nonionic polymers to be involved in strong cellulose interactions.

It has been shown in this study that it is possible to achieve fines retention while at the same time maintaining good fiber dispersion. Thus, it should be possible to achieve good sheet formation conditions while retaining large quantities of cellulosic materials, if optimum conditions can be reached in mill situations. These optimum conditions have been

achieved in the laboratory during this study, but nothing can be said about the attainability of these conditions in real mill situations. It is important to note here that the polymer addition levels used in this study were the same as are recommended by the polymer manufacturers for mill situations (104-106).

CONCLUSIONS

A comparison of cellulose fiber-to-fiber and fines-to-fiber interactions was conducted, with the purpose of establishing their similarities and/or differences as affected by simple electrolytes, polyelectrolytes, fines, pH, and degree of agitation.

Results of the comparison indicated that it was possible to maintain fines-to-fiber interactions, while at the same time substantially reducing fiber-to-fiber interactions. Under certain conditions of polyelectrolyte alone and polyelectrolyte plus electrolyte, it was found to be possible to maintain fines retention, while at the same additive concentration level, maintaining good fiber dispersion. These conditions could be maintained over a pH range of 5 to 9, for two extreme agitation conditions (gentle and severe), and for both a low and high fines addition level. This finding indicates that it may be possible in mill situations to achieve good sheet formation properties and also maintain good cellulose material retention.

The study presented evidence that cellulose fiber-to-fiber and fines-to-fiber interactions were influenced in the same manner by simple electrolyte additives. The degree of coagulation of the two systems was low until a critical concentration of electrolyte was reached, at which point the degree of coagulation was rapidly increased, with the coagulation maintained upon adding more electrolyte. The critical concentrations for both systems were the same.

The fiber-to-fiber interactions as influenced by polyelectrolytes were not dependent on pH over a pH range of 5 to 9, while the fines-to-fiber systems did show a pH dependence over this range, but only for systems of less than maximum fines retention. It is felt that this difference was not so much a result of basic differences in the two test systems, but rather a result of lower sensitivity in the detection system for the fiber-to-fiber interactions compared with the fines-to-fiber interactions.

Two extremes of agitation were evaluated as to the effect that variations in agitation had on fiber-to-fiber and fines-to-fiber interactions. These extremes in agitation had no effect under the influence of simple electrolytes; however, polyelectrolytes were much more dependent on agitation than were the simple electrolytes. Fiber-to-fiber systems required less polymer to achieve maximum flocculation at elevated agitation than at reduced agitation, indicating that collision frequency and potential barriers were controlling factors instead of the disruptive forces of turbulence. Fines were retained to a lesser degree at elevated agitation, indicating that the turbulence factors were more important than collision and energy factors.

It was concluded that the coagulating power of mono-, di-, and trivalent cations increased with increasing cation charge, following the Schulze-Hardy rule of colloid coagulation. La(+3) was a better coagulant than was Ca(+2) than was Na(+1).

For the polyelectrolytes, it was shown that the cationic polymer was a much more effective flocculant than the anionic or nonionic polymers.

There was little difference observed for the anionic and nonionic polymers. These results followed charge conditions of the materials, with the positively charged cationic polymer interacting more strongly with the negative cellulose than did either the negative or noncharged polymers.

Another important conclusion from this work is that the amount of fines present in a fiber slurry affected the degree to which the fiber slurry was flocculated. A 1.0% fines addition based on fiber weight produced no changes in fiber-to-fiber interactions as influenced by electrolytes or polymers. However, a 10% fines level of addition resulted in large increases in the degree of fiber flocculation by cationic polymer while maintaining the polymer concentration at which maximum flocculation occurred. This result was explained by the fact that the fines allowed the polymer bridges between fibers to become longer and more extensive as a result of polymer-fines-polymer structures. In effect, the fines extended the length of the polymer chains making the polymer a better flocculant.

And, finally, this study has demonstrated that the fiber optics light probe may be used by the paper industry in monitoring the degree to which the fibers of mill furnishes are forming fiber clusters or fiber networks. This program has presented evidence that the light probe is capable of following fiber interactions as affected by colloidal parameters, and that these colloidal influences are not overshadowed by the hydrodynamics of the fiber slurry under the conditions of the examination.

APPLICATION OF RESULTS

It is felt that there were two significant findings in the current program of importance to the paper industry. The usefulness of the fiber optics light probe for monitoring the degree of fiber cluster formation was demonstrated, and a comparison of fiber-to-fiber and fines-to-fiber interactions was completed.

It is felt by the author that the light probe can be put to good use by the paper industry for the purpose of monitoring the degree of fiber dispersion in papermaking furnishes. This is not to say that there are not any major problems, but the problems can be worked out. The three major problems encountered are concerned with the consistency of fiber slurry, the stapling of fibers to the light probe, and the velocity fluctuations of the fibers passing in front of the light probe.

This study has shown that fiber consistencies of 0.5 and 1.0% are workable with the light probe. Similarly, Muhonen (69) and Chiu (43) used the light probe effectively at fiber consistencies of 0.6 to 0.8%, and 0.1 and 0.7%, respectively. Consistency variations will affect the intensity of reflected light and thus light probe sensitivity, but most mill slurries fall into the region of workability of the light probe. The length of the slurry fiber, probe position, and flushing water rate are important in determining the degree to which fibers may staple to the light probe, cutting off transmitted and reflected light. Generally, the longer the fiber the more stapling will be a problem. Chiu's (43) system demonstrated the usability of the light probe with small groundwood fibers and long bleached softwood kraft fibers, while the current study worked

successfully at intermediate fiber lengths for bleached kraft aspen fibers. It is apparent that the stapling problem can be overcome for most fiber systems.

The problem of what the light probe detects is perhaps its biggest fault. The light reflected by a particle passing in front of the probe is dependent on the direction of its approach (parallel or perpendicular to the axis of the probe) and its velocity (69). Thus, it is felt that data between two probes at different machine locations cannot be made because of variations in slurry fiber velocity and direction profiles. However, as this study has demonstrated, useful fiber cluster formation data can be obtained from a light probe looking at the same area of furnish under the same flow conditions in the same geometric arrangement. To summarize, a papermakers slurry in a mill situation with the correct consistency and stapling conditions can be monitored by a fiber optics light probe as to fiber network formation tendencies as long as the test conditions remain constant for the purpose of comparisons.

The results of the fiber-to-fiber interactions compared with the fines-to-fiber interactions demonstrate important differences in the two systems under the same test conditions on a laboratory scale. These differences in interactions confirm that it is possible to achieve good fiber dispersion, while at the same time achieving good fines retention. If these two conditions can be reached in mill situations, then a sheet of uniform fiber distribution can be made while reducing fines materials escaping into mill white water systems. The attainment of these optimum conditions in the laboratory is in no way conclusive proof of obtaining similar results in mill situations, although it is conclusive proof that the optimum conditions do exist.

SUGGESTIONS FOR FUTURE WORK

One of the more significant findings coming from this program was that the fiber-to-fiber flocculation tendencies were dependent on the level of fines addition. The current study evaluated only a low fines addition where little influence was found and a high fines level where a large influence was noted. It would be useful to evaluate this fines influence in a more extensive way, so as to establish fines concentration levels of importance to fiber cluster formation. This type of study would not necessarily need carbon-14 fines for the tests. However, once a fines concentration is established that influences fiber interactions, then it would be useful to compare some of the fiber-to-fiber and fines-to-fiber interactions evaluated in the current work, using the same experimental techniques of this study. A study of this type would help clear up some of the extrapolations from laboratory work to mill situations.

It has been demonstrated that the two branched fiber optics light probe can be used to monitor fiber-to-fiber cluster formation tendencies. The next step then is to take the light probe and use it to monitor fiber systems on a pilot plant scale. A study of this type should be of great benefit in further demonstration of light probe use in mill situations.

There are lingering doubts as to what the light probe is actually observing. Of how much importance are the hydrodynamics of the slurry and of the colloidal properties of the fibers? A detailed study is needed to fully characterize the light probe in terms of fiber velocity profiles in the sense of establishing where hydrodynamic conditions begin to overshadow colloidal factors. A study of this type would make it possible

to evaluate agitation effects on fiber cluster formation without the problem of how much of the observed effects are a result of slurry hydrodynamic changes.

This study in comparison with other studies (43,69) has pointed out some definite differences in fiber-to-fiber interactions as affected by polymer additives and agitation times. It appears as if these differences may be a result of either the ability of the polymer as a flocculant or of changes in fiber type. Naturally, when one system is changed, the interactions with the second system would be different. Thus, it would be helpful to study polymer and fiber types under well-defined pH and agitation conditions to establish the degree of importance of polymer type and fiber type to polymer-fiber interactions.

It would be of interest to evaluate papermaker's alum in terms of its coagulating ability, since it is the major electrolyte additive used by the paper industry. The trivalent lanthanum system was used in this study because it does not demonstrate the complex polymeric structures that Al(+3) can generate. A study of this type would bring the laboratory work still closer to mill situations.

The effects of pH were observed for some of the fines systems, but not the fiber systems, probably as a result of low sensitivity of the light probe in following the small pH effects. An attempt to modify the testing conditions or detection equipment in order to follow pH effects of fiber-to-fiber interactions would be useful.

Mixing of polymer and cellulose materials was a concern in the test program, since it is known that the method of polymer mixing can influence its flocculating ability (71). The current study by-passed the problem by mixing all systems in a reproducible manner. Most polymer additives in mill situations are added as close to the forming wire as possible, and so a study evaluating polymer mixing methods and times would help establish optimum mixing methods and mixing times for particular fiber-polymer systems.

All test evaluations in the present study were conducted at room temperature. Since slurry temperatures on commercial paper machines are considerably higher than room temperature, a study of the effects of temperature on fiber-to-fiber and fines-to-fiber interactions would be useful. Such parameters as polymer adsorption and ion mobility are dependent on temperature, possibly resulting in changes in the extent that polymer bridge formation and the degree of electric double layer collapse.

It was suggested by Meyer (84) that it may be possible to obtain a more continuous output of fiber cluster formation tendencies by following the power requirement of the impeller in addition to using the fiber optics light probe. As the fibers interact and form more and larger clusters, more power would be required by the impeller to maintain a constant rpm value. Thus, the power requirement of the impeller should be proportional to the extent of fiber-to-fiber interactions. A program to determine the effectiveness of this new detection method would be of value to future studies of fiber-to-fiber interactions.

As pointed out in the body of this paper, two separate pulpings of aspen logs were conducted. The ability to disperse these two fiber batches was markedly different under similar test conditions, with batch I fiber showing larger standard deviations than did fiber batch II. Since these two fiber batches were pulped and bleached in as nearly the same ways as possible, the question is raised as to the variability between commercial pulps from day to day or even hour to hour. A program should be established to evaluate this variability in similarly pulped fibers as to the effects on fiber-to-fiber interactions. It is possible that some paper machine problems may be traced to variations in fiber-to-fiber interactions as a result of changes in day to day pulping procedures and processes.

And last, it is felt that the radioactively tagged carbon-14 fines technique has been and can be a very powerful tool in following fines-to-fiber interactions. Therefore, as suggested by Dickey (107) of the Institute staff, it is hoped that a program can be established for the purpose of having a continuous supply of carbon-14 fines and fibers on hand at the Institute.

ACKNOWLEDGMENTS

My special appreciation is expressed to my Thesis Advisory Committee: Dr. Dale G. Williams, Dr. Robert A Stratton, and Mr. Nai L. Chang. Special thanks is given to Dr. Williams for his special guidance and counselling as committee chairman. Appreciation is also given to Mr. Heribert Meyer for his help to me and committee members on certain technical areas concerning the fiber optics light probe and system hydrodynamics.

Thanks is given to Fred Sweeney and Don Beyer for their assistance in the construction and maintenance of the photographic equipment. Their work in keeping me supplied with film development chemicals was very helpful.

I would also like to thank Keith Hardacker for his support in designing and maintaining the electronics of the test equipment.

The support and friendship shown to me by the entire Institute staff and faculty, as well as by fellow students was truly appreciated.

A special thanks is given to Sue Glinski and Doreen Dimick who supplied many hours of work in typing this thesis.

My wife, Donna, deserves very special thanks for her total support throughout the program. Not only has she been a perfect wife and mother the past three years, but she helped me read an estimated 150,000 data points from developed photographic film, saving me many days of effort.

Finally, perhaps my strongest feeling of appreciation is extended to The Institute of Paper Chemistry for supplying the means for me to continue my education, as well as for its financial support.

LITERATURE CITED

1. Derjaguin, B., Acta Physiochimica U.R.S.S. 10:333(1939); Trans. Faraday Soc. 36:203(1946); Acta Physiochimica U.R.S.S. 12:181(1940).

2. Derjaguin, B., and Landau, L. D., Acta Physiochimica U.R.S.S. 14: 633(1941).

3. Verwey, E. J. W., Philips Research Repts. 1:33(1945).

4. Verwey, E. J. W., and Overbeek, J. T. G., Trans. Faraday Soc. 42B: 117(1946).

5. Walkush, J. C. The coagulation of cellulose pulp fibers and fines as a mechanism of retention. Doctor's Dissertation. Appleton, Wisconsin, The Institute of Paper Chemistry, 1970.

6. Han, S. T., and Chang, N. L., Tappi 52(4):688-93(April, 1969).

7. Huber, O., Wochbl. Papierfabr. 99(1):16-20(1971).

8. Hastbacka, K., and Nordman, L., Paperi Puu 45(6/7):353(1963).

9. Linke, W. F., Tappi 45(4):326(1962).

10. Mason, S. G., Pulp Paper Mag. Can. 49(13):99-104(1948).

11. Swanson, J. W. Effects of soluble nonfibrous materials on formation and consolidation of paper webs. In Trans. of the Symposium on Consolidation of the paper web. p. 741-72. London, Tech. Sect. Brit. Paper and Board Makers' Assoc., 1966.

12. Ref. (11), p. 752.

13. Williams, D. G., Tappi 56(12):144-7(1973).

14. Bozhkov, I., Tseluloza Khartiya 3(6):10-13(Nov./Dec., 1972).

15. Finkel'shtein, G. E., Bumazh. Prom. 6:10-11(1972).

16. Pummer, H., Tappi 56(4):112-15(April, 1973).

17. Frankle, W. E., and Penniman, J. G., Jr. New technology has the potential of enormously improving the cost, quality, and quality uniformity of paper mill operation. Croton-on-Hudson, New York, Pen Kem Company, 1973.

18. Sortwell, E. T., Paper Technol. 13(1):41-8(T25-35)(Feb., 1972).

19. Nerelius, L., Norman, B., and Wahren, D., Tappi 55(4):574-80(April, 1972).

20. Rubin, M. M., Paper Trade J. 101(6):39-43(Aug., 1935).

21. Strachan, J., Paper Maker 89:Ts 33-4(1935).

22. Strazdens, E., Tappi 55(12):1691(1972).

23. Ansart, M., and Manguin, H., ATIP Rev. 24(2):61-6(1970).

24. Britt, K. W., Tappi 56(3):83-6(1973).

25. Linke, W. F., Tappi 51(11):59A(1968).

26. McKenzie, A. W., Appita 22(3):82-6(1968).

27. Wollwage, J. C. The flocculation of papermaking fibers. Doctor's Dissertation. Appleton, Wisconsin, The Institute of Paper Chemistry, 1938.

28. Das, B. S., and Lomas, H., Pulp Paper Mag. Can. 74(8):95-100(Aug., 1973).

29. Ogiwara, Y., and Kubota, H., J. Polymer Sci., Part A-1, 10(4):1001 (1972).

30. Vallette, P., and Lafaye, J. F., ATIP Rev. 24(2):75-9(1970).

31. LaMer, V. K., and Smellie, R. H., Jr., J. Colloid Sci. 19:291(1964).

32. Belodis, V., Appita 18(5):184(1965).

33. Steenberg, B., and Wahren, D., Appita 18(5):180-3(1965).

34. Swanson, J. W. Unpublished work, 1971.

35. Persinger, W. H., Jr. Scale of flocculation for fully developed turbulent tube flow of dilute fiber suspensions. Doctor's Dissertation. Appleton, Wisconsin, The Institute of Paper Chemistry, 1974.

36. Anderson, O., Svensk Papperstid. 64:517-18(1961).

37. Chang, M. Y., and Robertson, A. A., Pulp Paper Mag. Can. 68(9):T438-44 (Sept., 1967).

38. Anderson, O., Svensk Papperstid. 69(2):23-31(1966).

39. May, M. M. Unpublished work, The Institute of Paper Chemistry, 1965.

40. Voelker, M. H. Unpublished work, The Institute of Paper Chemistry, 1957.

41. MacLaurin, D. J., Peckham, J. R., Elston, R. E., and Voelker, M. H. Unpublished work, The Institute of Paper Chemistry, 1954.

42. Hoffman, G. R. Unpublished work, The Institute of Paper Chemistry, 1966.

43. Chiu, K. Forces of fiber flocculation and fines retention provided by polymers as influenced by hydrodynamic shear. Unpublished work, The Institute of Paper Chemistry, 1973.

44. Hubley, EC. E., Robertson, A. A., and Mason, S. G., Can. J. Res. 28(8):770-87(1950).

45. Weast, R. C., and Selby, S. M., eds. Handbook of chemistry and physics. 47th ed. Cleveland, Ohio, Chemical Rubber Co., 1962.

46. Gavelin, G., Pulp Paper Mag. Can. 55(3):191-200(March, 1954).

47. Hall, D. H., Tappi 42(8):178-80A(1959).

48. Tester, J. W., Tappi 44(4):148-52A(1961).

49. Whims, L. J., Paper Trade J. 146(38):50, 52(1962).

50. Chang, N. L. Personal communication, 1973.

51. King, C. A. The interaction of gases with composites. Master's Dissertation. Blacksburg, Va., Virginia Polytechnic Institute and State University, 1972.

52. Gostkowski, K., Zeszyty Nauk. Politech. Slash. Chem. 3:51-6(1954).

53. Moore, W. J. Physical chemistry. 3rd. ed. p. 328. New York, N.Y., Prentice-Hall, 1964.

54. Perrin, J. J., Chem. Phys. 2:601(1904).

55. Clapp, R. J. An investigation of the relationship between carboxyl content and zeta potential. Doctor's Dissertation. Appleton, Wisconsin, The Institute of Paper Chemistry, 1972.

56. Helmholtz, --, Wied. Ann. 7:337(1879).

57. Gouy, --, J. Phys. Chem. 9:457(1910).

58. Chapman, --, Phil. Mag. 25:475(1913).

59. Stern, O., Z. Electrochem. 30:508-16(1924).

60. Sheludko, A. Colloid chemistry. 3rd ed. p. 141-72. New York, Elsevier Publ. Co., 1966.

61. Adamson, A. W. Physical chemistry of surfaces. 2nd ed. p. 210-18. New York, N.Y., Interscience, 1967.

62. Williams, D. G., and Swanson, J. W., Tappi 49(4):147-51(1966).

63. Beasley, D. E., Pulp Paper 27(5):58-60(1953).

64. Erspamer, A., Tech. Assoc. Papers 23:132-7(1940).

65. Dobbins, R. J., Tappi 53(12):2284(1970).

66. Goring, D. A. I., Pulp Paper Mag. Can. 67:T519(1966).

67. Anderson, D. D., and Branswick, J. J., Svensk Papperstid. 64(13): 493-9(1961).

68. Hukki, R. T., and Rinne, R., Paperi Puu 36(4a):129(1954).

69. Muhonen, J. M. The forces of fines retention in groundwood pulp provided by polymer materials. Unpublished work, The Institute of Paper Chemistry, 1972.

70. LaMer, V. K., and Smellie, R. H., Jr., J. Colloid Sci. 13(6):589-99 (1958).

71. Fleer, G. J. Polymer adsorption and its effects on colloid stability. Doctor's Dissertation. p. 23-6. Wageningen, Netherlands, Agricultural University, 1971.

72. Overbeek, J. T. G., Disc. Faraday Soc. 42:7-13(1966).

73. Robertson, A. A., and Mason, S. G., Pulp Paper Mag. Can. 55:C263(1954).

74. Sanders, H. T. An investigation of fiber consistency distributions in turbulent tube flow. Doctor's Dissertation. Appleton, Wisconsin, The Institute of Paper Chemistry, 1970.

75. Moore, E. E., Tappi 56(3):71(March, 1973).

76. Strazdins, E., Tappi 53(1):80(Jan., 1970).

77. Hahn, H. H., and Stumm, W. Coagulation by He(III). The role of adsorption of hydrolyzed aluminum in the kinetics of coagulation, adsorption from aqueous solution. Am. Chem. Soc., Adv. in Chem. Series No. 79, Washington, D.C., Am. Chem. Soc., 1968.

78. LaManna, C., and Mallet, F. M., J. Bact. 67:503(1954).

79. Coulter Electronics Industrial Div. Coulter Counter Industrial Model B instruction manual. Franklin Park, Illinois.

80. Graham, L. Personal communication, 1974.

81. Peckham, J. Personal communication, 1974.

82. Shyluk, W. P., and Stow, F. S., Jr., J. Appl. Polymer Sci. 13:1023(1969).

83. Beckman Instruments Inc. Model LS-100 Liquid Scintillation Counter, instruction manual 1553-D. Fullerton, CA., 1963.

84. Meyer, H. Personal communication, 1974.

85. Casey, J. P. Pulp and paper chemistry and technology. 2nd ed. Vol. 1. p. 557. New York, N.Y., Interscience, 1960.

86. Kruyt, H. R., ed. Colloid science. Vol. 1. p. 304. New York, N.Y., Elsevier, 1952.

87. Sparnaay, M. J., Rec. Trav. Chim. 78:680(1959).

88. Daluja, K. L., and Srivastava, S. N., Kolloid Z. 232:781(1969).

89. Schenkel, J. H., and Kitchener, J. A., Disc. Faraday Soc. 42:161(1966).

90. Stryker, L. J., and Matijevic, E., Kolloid Z. 233:912(1969).

91. Goring, D. A. I., and Mason, S. G., Can. J. Research B-28:307-22, 323-38 (June, 1950).

92. Thode, E. F., and Htoo, S., Tappi 38:705-9(1955).

93. Ostwald, --, and Lorenz, --, Kolloid Z. 32:119-37(1923).

94. LaMer, V. K., and Healey, T. W., Pure Applied Chem. (Aust.) 13:112-33 (1963).

95. Fischer, E. W., Kolloid Z. 160:120(1958).

96. Bagchi, J., J. Colloid Interface Sci. 47(1):86(April, 1974).

97. Heller, W., and Pugh, T. L., J. Polymer Sci. 47:203-17(1960).

98. LaMer, V. K., Smellie, R. H., Jr., and Lee, P.-K., J. Colloid Sci. 12 (6):566(1957).

99. Meyer, H. Personal communication, 1973.

100. Becher, J. Personal communication, 1974.

101. Andrews, B. Personal communication, 1974.

102. Stratton, R. A. Personal communication, 1974.

103. Huggins, M. L. Physical chemistry of high polymers. New York, N.Y., John Wiley and Sons, 1958.

104. American Cyanamid Co. Product Bulletin D118, Accura: 24+, Jan., 1969.

105. American Cyanamid Co. Product Bulletin, Mining chemicals, superfloc flocculants. June, 1966.

106. American Cyanamid Co. Product Bulletin, WTC-36, Magnifloc 5600. October, 1971.

107. Dickey, E. E. Personal communication, 1974.

108. Cluley, H. J., Analyst 81:170(1962).

APPENDIX I

PREPARATION AND TREATMENT OF CARBON-14 FINES

In the summer of 1966, Walkush (5) intermittently exposed twenty triploid aspen seedlings to a total of 8.0 mC_i of carbon-14 dioxide to determine if this technique was feasible for obtaining carbon-14 cellulose. This technique yielded a material of low specific activity, so that in the summer of 1967, the growing process was repeated with 125 mC_i of carbon-14 dioxide. The details of this second growing cycle, which are essentially the same as the first, are discussed below.

A growing chamber was constructed to contain the radioactive atmosphere by covering a large wooden frame with 10-ml polyvinyl chloride construction plastic. It should be noted that this plastic had the lowest carbon dioxide diffusion coefficient of any available. It would be better to use glass if the added expense could be justified. The outside dimensions of the chamber included a 60 by 70-inch base, 60-inch sides, and a 72-inch center height. One side of the chamber was removable for easy access to the trees. The door frame and all other joints were carefully sealed to prevent excessive leakage of the radioactive atmosphere.

A total of 30 seedlings were individually potted and placed in a shallow trough in the bottom of the chamber for easy watering. Fifteen, two-year-old Pinus resinosa; ten, three-year-old Populus tremuloides treated the previous summer but not harvested; and five of the poplar seedlings treated and harvested the previous summer were treated in the cycle.

The treatment procedure was essentially the same for both growing cycles. At the beginning of each week throughout the summer, the chamber was first closed and sealed tightly and then purged with carbon dioxide free air for ca. 4 hours to reduce photosynthesis. Compressed air was scrubbed in a dilute alkali solution and fed through a stopcock placed in the wooden frame. The chamber was vented through another stopcock. The effectiveness of this purging process in displacing the carbon dioxide in the chamber was not determined, however.

After the purge was completed, a carbon-14 dioxide generator was attached to the inlet stopcock. The carbon-14 dioxide was generated in a round-bottom flask by addition of dilute acid to aqueous barium carbonate containing carbon-14. The amount of carbon-14 dioxide generated varied from 10-20 mC_i as seen in the treatment schedule shown in Table V. Additional carbon dioxide was generated, also at this time, to maintain the overall concentration at 0.03% which is the normal atmospheric concentration.

TABLE V

TREATMENT SCHEDULE

Treatment Number	Date Started	Purge Time, hr	Carbon-14 Dioxide Added, mC_i	Treatment Period, hr
1	6/26/67	4	10.0	78
2	7/06/67	10	10.0	134
3	7/17/67	9	10.0	58
4	7/24/67	3	10.0	58
5	7/31/67	5	20.0	58
6	8/07/67	4	10.0	58
7	8/14/67	4	20.0	58
8	8/21/67	4	20.0	58
9	8/28/67	4	15.0	58

The background radiation level in the chamber was monitored during the first five treatments of 1967 with a Geiger-Mueller tube positioned in the wooden frame. The results presented in Fig. 30 generally show the rapid build-up of background radiation during the first hour after the carbon-14 dioxide was generated, the gradual decay due to photosynthesis during the daylight hours, and a small increase during the second day. There are two possible explanations for the second peak: either the trees respired some of the carbon-14 dioxide assimilated the first day, and/or the increasing temperature inside the chamber released carbon-14 dioxide adsorbed in the water. It can also be seen that at the end of the usual growing period of 2.5 days, the radiation level was almost reduced to the background level. It should also be noted that the initial radiation level increased with each treatment monitored which indicated the trees were assimilating and retaining carbon-14.

The first treatment curve is different than the next three curves because the Geiger-Mueller tube counting voltage was erroneously set too high which causes an excessive amount of ionization of the counting tube gas.

In the first growing cycle during 1966, a second generation of carbon dioxide was performed 7-8 hours after the carbon-14 dioxide was generated to increase the atmospheric carbon dioxide concentration to 0.5% to sustain photosynthesis. This was also done in the first three feedings of 1967, but there was some question as to the value of this process because it was thought there could be sufficient diffusion and leakage of carbon dioxide into the chamber to maintain tree growth. Since the second maximum in the radiation curves also indicated there was carbon-14 dioxide in the system, it was decided to eliminate this step in the fourth treatment. As can be

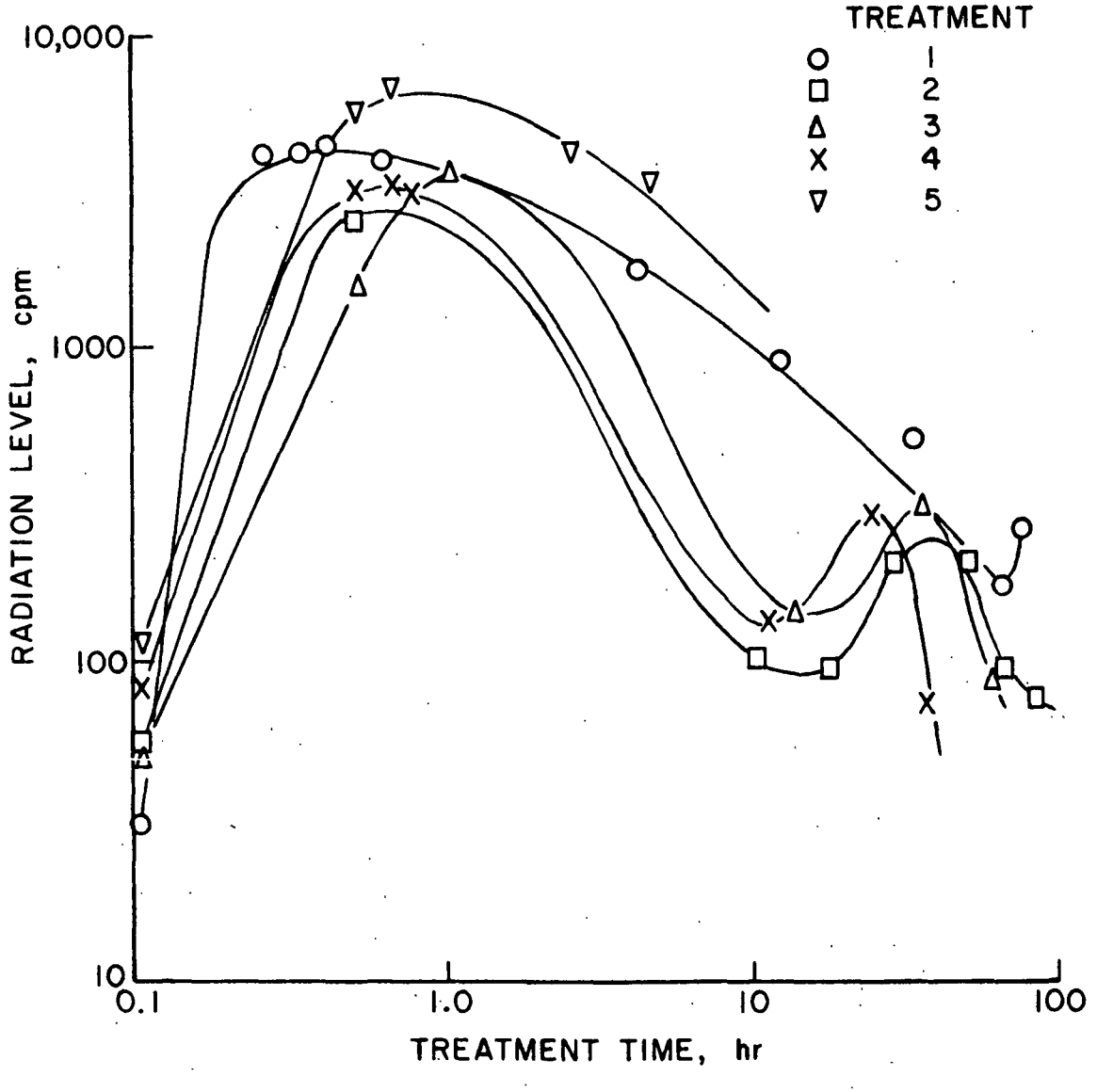


Figure 30. Growing Chamber Radiation Level

seen in Fig. 30, the only effect of the elimination was a slight shift in the second minimum to a shorter time. This meant the carbon-14 dioxide was assimilated sooner which was advantageous because there was less chance of loss from the chamber. Therefore, it was decided to eliminate this step in the remaining treatments.

In the fifth treatment, the initial dosage was doubled because the 10.0 mC_i carbon-14 dioxide was readily assimilated in the first day. A few radiation counts were made during the first day, but failure of the Geiger-Mueller tube prevented any further measurements. Since a replacement was not readily available, the same treatment procedure used in the fourth addition was used in the remaining feedings.

Since the growing season was rapidly closing during the last treatment, it was decided to increase the dosages as listed in Table V. It would have been better to have had the higher dosages during the peak growing time earlier in the season rather than as was done when the cell reproduction rate was beginning to slow down.

An estimate of the amount of carbon-14 assimilated by the trees during each treatment was obtained by scrubbing the chamber air in a concentrated barium hydroxide solution. This was essentially the same procedure described above for the initial purge but in the reverse direction. It was started some two and one half days after the carbon-14 dioxide was generated prior to opening the chamber to the atmosphere. Total purge time was at least 4.0 hours.

After the growing chamber was purged, the side door was removed, and the trees were allowed to grow in the open atmosphere for the remainder of the week. The procedure was then repeated each week throughout the summer.

The estimate of the assimilation rate was obtained by filtering, drying, weighing, and measuring the specific activity of the radioactive barium carbonate formed in the latter purge. The specific activity was determined by the same procedure used by Cluley (108). The results for each of the treatments are summarized in Table VI.

TABLE VI

CARBON-14 DIOXIDE RECOVERY

Treatment Number	Carbon-14 Dixoide Added, mC_i	Radioactive Barium Carbonate Recovered, g	Specific Activity,[a] $\mu C_i/g$	Total C-14 Recovered, μC_i	Recovery, %
1	10.0	3.26	6.89	22.45	0.22
2	10.0	5.01	1.00	5.01	0.05
3	10.0	6.65	1.76	11.70	0.12
4	10.0	7.40	2.20	16.25	0.16
5	20.0	9.59	4.12	19.28	0.09
6	10.0	9.09	2.65	24.10	0.24
7	20.0	10.54	4.47	47.20	0.24
8	20.0	3.03	3.84	11.62	0.06
9	15.0	20.19	6.61	133.50	0.90

[a]Based on a counting efficiency of 90.0%.

It can be noted that of the total 125 mC_i carbon-14 dioxide only 291 μC_i were recovered which would indicate a total assimilation rate of 99.8%. However, this does not mean all of the carbon-14 was consumed by the trees since there was some unaccountable loss by diffusion and water adsorption. Also, the actual recovery efficiency of the purge was not known. Therefore, no specific conclusions can be drawn from these results.

Nine of the aspen seedlings treated in both cycles were harvested by cutting the primary branch off near the main stem. The trees would then sprout a new branch the following summer and continue growing. The other trees were kept in the pots, stored over the winter, and retreated again by other workers the next summer to build up an inventory of radioactive wood.

The specific activity of the different tree components was determined with the scintillation counter described previously. The solid samples were suspended in a counting cocktail made with colloidal silica, toluene, and PPO phosphor. The procedure was the same that Cluley used for analyzing solid barium carbonate samples (108).

The counting efficiency in this cocktail was determined by addition of standard carbon-14-toluene to two samples having a fairly large difference in external standard ratios. A linear relationship was assumed in calculating the efficiency curve. Counting efficiency varied from 70-80% depending on the external standard ratio. The average specific activity determinations for the various tree components are summarized in Table VII.

As can be seen, all of the tree components were tagged with carbon-14. It should be noted that the branch tips had consistently higher specific activities than the other positions because they were not diluted by the old untagged wood. The high specific activity of the extractives is probably due to the immature nature of the wood which usually has a very high extractive content compared to normal pulpwood. Young trees abound in pectin materials which are removed as extractives.

TABLE VII

SPECIFIC ACTIVITY OF RADIOACTIVE ASPEN

Component	Quantity, g	Specific Activity, $\mu C_i/g$
Wood total	84.3	13.88
Branch base	--	6.07
Branch middle	--	14.21
Branch tip	--	21.17
Leaves	--	9.71
Bark	71.0	16.81
Extractives		
Alcohol:benzene	5.08	38.2
Alcohol	3.67	32.9
Hot water	3.48	27.9

This technique was shown to be a rather simple method for radioactively tagging large quantities of wood. The method can be summarized as three easy steps: purging the system of carbon dioxide, addition of radioactive carbon dioxide, and removal of unassimilated carbon-14 after a 2-3 day growing period. However, it could be improved by building an air-tight chamber that contained only the leaves and branches because this would reduce carbon-14 loss to the atmosphere and eliminate adsorption in the water that was used to maintain the soil moisture content. This later problem is thought to be the most serious and should be eliminated in future growing cycles.

APPENDIX II

RADIOACTIVE ASPEN KRAFT PULPING CONDITIONS

A summary of the pulping conditions used to prepare the radioactive pulp is presented in Table VIII.

TABLE VIII

RADIOACTIVE ASPEN PULPING CONDITIONS

Wood:	
Airdry weight, g	88.5
Moisture content, %	5.8
Ovendry weight, g	83.4
Liquor:	
Liquor-to-wood ratio	6:1
Active alkali, g/l as NaOH	40.2
Sulfidity, %	20.0
Cook:	
Maximum temperature, °C	170
Time to temperature, min	120
Time at temperature, min	75
Yield:	
Pulping, %	48.8
Bleaching, %	88.0
Total, %	42.8

APPENDIX III

BLEACHED KRAFT ASPEN PULPING PROCESSES

A procedure was developed in conjunction with John Peckham of the Institute's pulp laboratory for the purpose of cooking and bleaching the aspenwood to be used in the experimental program. The procedure involved a kraft digestion of an aspenwood log, followed by an acidified sodium chlorite bleaching of the pulp. Two separate pulping and bleaching sequences were conducted during the experimental program. These two formulations are described below.

The first aspenwood log obtained from John Peckham was debarked and chipped, with 22 pounds of chips obtained after screening. The chips were found to have an oven-dried moisture content of 15%. The chips were next pulped in an Institute digester using cooking times and conditions presented in Table IX.

TABLE IX

PULP COOKING CONDITIONS

Time, min	Temperature, °C		Pressure, psi
	Proposed	Actual	
10:00	25	22	0
10:15	50	48	0
10:30	75	75	5
10:45	100	100	20
11:00	125	125	55
11:15	150	150	90
11:30	169	169	105
11:35	172	173	110
11:40	172	176	105
11:45	172	174	102
11:50	172	172	101
11:55	172	171	101
12:00	172	172	101
12:05	172	172	102
12:10	172	173	102
12:15	172	173	102
12:20	172	172	102
12:25	172	172	102
12:30	172	172	102
12:35	172	172	102

The wood, water, and chemicals used in the pulping process are listed in Table X.

TABLE X

DIGESTER MATERIALS

Chip weight, wet, g	8991
Chip weight, o.d., g	7950
Water in chips, g	1041
Active alkali as Na_2S, %	17
Sulfidity, %	30
Water ratio, ml/g o.d. wood	4.5
NaOH, l	4.325
Na_2S, l	3.920
Water, l	26.624

After the cook was completed, digester blowdown was accomplished at 80 psi. The pulp was washed for ten minutes, drained, and washed twice at five minutes each. Next, the pulp was screened in a Valley diaphragm screen using a screen cut size of 0.009 inch. The pulp was then dried in a laundry-type centrifuge using a muslin cloth bag, followed by a single pass through a laboratory disintegrator in order to break up large clumps of pulp.

The pulp was bleached in lots of 2547 grams of wet pulp. The pulp and bleaching chemicals were placed in a polyethylene bag and submerged in a 50°C water bath for four hours. The materials added to the bags are listed in Table XI.

TABLE XI

BLEACHING MATERIALS

Pulp, wet, g	2547
Pulp, dry, g	800
Water from pulp, g	1747
Chemical solution, ml	6333
Water, ml	6253
Sodium chlorite, g	40
Glacial acetic acid, ml	40

The polyethylene bag was rotated and the pulp agitated once each hour. After the four-hour bleaching period, the pulp was washed sufficiently to remove all bleaching chemicals. All individual pulp batches were combined and washed for 15 minutes in the large stirring tank in the pulp laboratory. The washed pulp was dried on the laundry-type centrifuge for 10 minutes and stored in a large polyethylene bag at 40°F without preservative.

The final stage of the pulp preparation was the classification of the pulp. The pulp was classified on the Institute's web former with the assistance of Bruce Andrews of the Institute staff. Two passes were made on the web former using a 70 × 54 semitwill bronze wire. The pulp was then stored in a polyethylene bag at 40°F until required for use. Formaldehyde preservative was added by saturating a piece of blotter stock with the formaldehyde and placing the blotter stock in the bag with the pulp.

The final pulp was 19.6% dry fiber by weight, meaning that approximately eight pounds of dry fiber was obtained from the original 17.5 pounds of dry fiber added to the digester.

After the first batch of test fibers was exhausted, it became necessary to formulate a second batch of test fiber. Similar pulping and bleaching procedures were used for the second aspenwood log as for the first case. The process involved a kraft digestion of an aspenwood log, followed by an acidified sodium chlorite bleaching of the pulp. The log was debarked and chipped, with 10.635 kg of chips obtained after screening. The chips were found to have an oven-dried moisture content of 19% by weight. However, only 8.295 kg of chips could be used, due to a limitation in digester size. The chips were pulped in an Institute digester using cooking times and conditions as presented in Table XII. Table XII also contains the materials placed into the digester. After the cook was completed, the digester basket was removed and the pulp collected, followed by two washings for ten minutes each. The pulp was stored overnight in the water slurry form. Next, the pulp was screened in a Valley diaphragm screen using a screen size of 0.009 inch. The pulp was dried in a laundry-type centrifuge using a muslin cloth bag, followed by a single pass through a laboratory disintegrator. The disintegrated pulp was stored in a large polyethylene bag in a 40°F refrigerator for one night, or until bleaching was initiated.

The pulp and bleaching chemicals were sealed in a polyethylene bag and submerged in a 50°C water bath for four hours, being rotated and mixed on each hour. The chemicals consisted of 40 g of sodium chlorite dissolved in 6250 ml of water, to which was added 40 ml of glacial acetic acid. After the four-hour bleaching period, the pulp was washed sufficiently to remove all bleaching chemicals. All individual batches were combined and washed twice for 15 minutes in the large stirring tank in the pulp laboratory. This pulp slurry was stored overnight until drying could be initiated.

The washed pulp was next dried on a laundry-type centrifuge for ten minutes and stored in a large polyethylene bag at 40°F without preservative.

TABLE XII

DIGESTER COOKING CONDITIONS AND MATERIALS

Cooking Conditions

Time, min	Temperature, °C		Pressure, psi
	Proposed	Actual	
2:00	25	27	--
2:15	50	64	--
2:30	75	88	--
2:45	100	99	--
3:00	125	127	24
3:15	150	152	60
3:30	172	173	106
3:35	172	173	106
3:40	172	172	104
3:45	172	172	104
3:50	172	172	105
3:55	172	172	106
4:00	172	172	106
4:05	172	172	105
4:10	172	172	104
4:15	172	171	104
4:20	172	172	104
4:25	172	173	104
4:30	172	172	102
4:35	172	172	103

Digester Materials

Chips, wet, g	8295
Chips, dry, g	6720
Water from chips, ml	1575
Active alkali as Na_2S, %	17
Sulfidity, %	30
Water ratio, ml/g dry wood	4.5
NaOH, ml	3653
Na_2S, ml	4390
Water, ml	20762

The final stage in the fiber preparation was the classification of the pulp on the Institute web former. The pulp was classified on the web former by Jim Tierney of the Institute staff. Two passes were made on the web former using a 70 × 54 semitwill bronze wire. The classified pulp was then stored in a large polyethylene bag at 40°F until required for use. Formaldehyde preservative was added by saturating a piece of blotter stock with the preservative, the blotter stock being placed in the sealed polyethylene bag with the fibers. The completed fiber system was 22.5% dry fiber by weight, meaning that 3380 ovendry grams of fiber were obtained from the initial 8295 grams placed in the digester. This yield of 41% compares with a yield of 46% for the first batch of test fibers.

APPENDIX IV

PHYSICOCHEMICAL CHARACTERIZATION OF SYSTEM TEST FIBERS

The data presented in Table II in the body of this paper were obtained by the Institute's analytical group with the following methods. The sugar contents were taken via a method presented in Tappi 53(2):257(Feb., 1970), while the carboxyl content methods were from TAPPI T 237 su-63. For the carboxyl determinations, the sample was prewashed with 0.1N HCl as under the sodium bicarbonate-sodium chloride method. The actual carboxyl was monitored by the methylene blue method. All values represent single determinations.

The raw data for the specific area and volumes are presented in Table XIII for fiber batch I three months after pulping, fiber batch I nine months after pulping, and fiber batch II immediately after pulping, respectively.

The raw data obtained for the fiber length and width distributions is presented in Tables XIV and XV, respectively.

TABLE XIII

FIBER SPECIFIC SURFACE AREA AND SPECIFIC VOLUME DATA

System Description	Pressure Drop, cm water	Filtration Resistance $R \times 10^{-8}$, cm/g	Specific Surface $\langle \bar{S}_w \rangle$, sq cm/g	Specific Volume $\langle \bar{v} \rangle$, cc/g	Compressibility Function[a], $C = MP^n$	
					M	N
Bleached kraft aspen fibers (batch I — 3 months after pulping)	10	0.40	10,500	2.92	0.00149	0.381
	20	0.50				
	30	0.58				
	40	0.64				
	50	0.70				
	60	0.76				
	70	0.82				
	80	0.87				
	90	0.92				
Bleached kraft aspen fibers (batch I — 9 months after pulping)	10	0.36	9,900	2.70	0.00143	0.378
	20	0.43				
	30	0.48				
	40	0.53				
	50	0.58				
	60	0.62				
	70	0.66				
	80	0.69				
	90	0.73				
Bleached kraft aspen fibers (batch II — immediately after pulping)	10	0.45	11,600	2.76	0.00128	0.396
	20	0.61				
	30	0.69				
	40	0.79				
	50	0.84				
	60	0.93				
	70	1.00				
	80	1.06				
	90	1.11				

[a] Where C is the pad concentration in g/cc, P is the compacting pressure in dynes/sq cm, and M and N are empirical constants in consistent units.

TABLE XIV

RAW DATA FOR FIBER LENGTH DETERMINATIONS

Interval, mm	Frequency	(a) Frequency, %	(b) Average Length, mm	a • b	a • b²
		Fiber Batch I			
0.1-0.3	25	3.1	0.2	0.620	0.1240
0.3-0.5	105	13.0	0.4	5.200	2.0800
0.5-0.7	167	20.7	0.6	12.420	7.4520
0.7-0.9	198	24.6	0.8	19.680	15.7440
0.9-1.1	160	19.9	1.0	19.900	19.9000
1.1-1.3	91	11.3	1.2	13.360	16.2720
1.3-1.5	38	4.7	1.4	6.580	9.2130
1.5-1.7	21	2.6	1.6	4.160	6.6560
1.7-1.9	1	0.1	1.8	0.180	0.3240
Totals	806	100.0		82.300	77.7640

Arithmetic average fiber length = 0.83 mm
Weighted average fiber length = 0.95 mm

		Fiber Batch II			
0.0-0.1	--	--	0.05	--	--
0.1-0.3	4	0.4	0.2	0.08	0.016
0.3-0.5	67	6.5	0.4	2.60	1.040
0.5-0.7	196	19.2	0.6	11.52	6.912
0.7-0.9	311	30.5	0.8	24.40	19.520
0.9-1.1	254	24.9	1.0	24.90	24.900
1.1-1.3	144	14.1	1.2	16.92	20.304
1.3-1.5	37	3.6	1.4	5.04	7.056
1.5-1.7	7	0.7	1.6	1.12	1.792
1.7-1.9	1	0.1	1.8	0.18	0.324
Totals	1021	100.0		86.76	81.864

Arithmetic average fiber length = $\Sigma ab/100$ = 0.87 mm
Weighted average fiber length = $\Sigma \bar{a}\bar{b}^2/\Sigma \underline{a}\underline{b}$ = 0.94 mm

TABLE XV

RAW DATA FOR FIBER WIDTH DETERMINATIONS

Fiber Widths, μm

Fiber Batch I

12.5	10.0	12.5	22.5	22.5
20.0	20.0	12.5	20.0	25.0
7.5	7.5	20.0	20.0	27.5
12.5	20.0	17.5	15.0	25.0
10.0	12.5	10.0	22.5	17.5
12.5	17.5	80.0	25.0	15.0
20.0	20.0	20.0	12.5	25.0
20.0	15.0	12.5	10.0	12.5
17.5	17.5	17.5	20.0	20.0
17.5	20.0	17.5	17.5	12.5
17.5	15.0	20.0	12.5	15.0
17.5	15.0	12.5	20.0	17.5
17.5	12.5	10.0	17.5	20.0
20.0	75.0	17.5	22.5	12.5
20.0	15.0	15.0	12.5	15.0
15.0	17.5	7.5	17.5	17.5
20.0	22.5	22.5	12.5	77.5
15.0	12.5	22.5	25.0	12.5
22.5	20.0	15.0	12.5	12.5
15.0	15.0	20.0	15.0	22.5
17.5	10.0	17.5	20.0	12.5
17.5	12.5	10.0	22.5	12.5
10.0	22.5	22.5	25.0	17.5
				20.0

Arithmetic average fiber width including vessels = 2140 μm 116 = 18.4 μm
Arithmetic average fiber width without vessels = 1908 μm 113 = 16.9 μm

Fiber Batch II

66.0[a]	24.0	19.2[a]	13.2	31.2
14.4	25.2	96.0[a]	16.8	13.2[a]
16.8	88.4	13.2	9.6	76.8[a]
15.6	18.0	14.4	25.2	14.4
18.0	9.6	13.2	20.4	18.0[a]
14.4	14.4	14.4	14.4	74.4[a]
12.0	16.8	13.2	15.6	13.2
16.8	13.2	18.0	8.4	14.4
21.6	18.0	10.8	14.4	27.6
19.2	10.8	14.4	15.6	15.6
14.4	12.0	10.8	15.6	8.4
14.4	82.8[a]	25.2	15.6	20.4
16.8	14.4	16.8	15.6	16.8
15.6	18.8	16.8	20.4	19.2
14.4	26.4	19.2[a]	14.4	8.4
10.8	16.8	62.1[a]	19.2	12.0
28.8	20.4	20.4	27.6	12.0
15.6	28.8	20.4	18.0	28.8
19.2	20.4	10.8	25.2	
8.4	9.6	13.2	21.6	
24.0	10.8	12.0	19.2	

[a]Vessel element.

Arithmetic average fiber width, $\underline{w}$ = 15.9 μm
Arithmetic average fiber width including vessel elements, $\underline{w}$ = 20.4 μm

APPENDIX V

FIBER-TO-FIBER DATA REDUCTION

A typical set of basic data is listed in Table XVI. These data are fed into the computer program given (p. 149-151) just after the data points (Table XVI), with a typical computer printout (p. 152) presented after the computer program.

TABLE XVI

TYPICAL DATA SET FOR FIBER-TO-FIBER INTERACTIONS

Number	Value	Number	Value	Number	Value
1	4	35	4	68	3
2	4	36	1	69	4
3	3	37	2	70	3
4	3	38	6	71	3
5	5	39	3	72	3
6	5	40	4	73	4
7	4	41	7	74	4
8	4	42	4	75	5
9	4	43	5	76	4
10	4	44	3	77	4
11	5	45	4	78	3
12	3	46	6	79	5
13	4	47	5	80	3
14	4	48	4	81	4
15	4	49	4	82	4
16	5	50	3	83	3
17	5	51	3	84	4
18	4	52	4	85	4
19	0	53	8	86	6
20	4	54	4	87	5
21	5	55	3	88	4
22	3	56	4	89	3
23	5	57	3	90	4
24	6	58	4	91	3
25	3	59	5	92	3
26	3	60	4	93	7
27	2	61	1	94	4
28	6	62	4	95	4
29	5	63	5	96	5
30	5	64	4	97	2
31	8	65	5	98	5
32	4	66	6	99	6
33	5	67	3	100	6
34	5				

COMPUTER PROGRAM FOR EVALUATION OF FIBER-TO-FIBER INTERACTIONS

```
/JOB GO,TIME=10
      DIMENSION F(300),D(80),LINE(20)
      DIMENSION HEAD(20)
      INTEGER F
1     READ(5,8000) HEAD
 8000 FORMAT(20A4)
      WRITE(6,8001) HEAD
 8001 FORMAT('1',20A4)
      READ(5,9001) XMIN,CLINT,NINT
 9001 FORMAT(2F10.4,I5)
      XMAX = NINT*CLINT + XMIN
      IF(NINT - 100) 3,3,2
    2 WRITE(6,9002) NINT
 9002 FORMAT(1H0,I5,' IS TOO MANY CLASS INTERVALS. (100 MAX)')
 9003 FORMAT('0DATA POINT=',E16.8,' IS OUT OF THE RANGE')
      GO TO 1
    3 DO 4 I = 1,NINT
    4 F(I) = 0
      S = 0.
      S2 = 0.
      ND = 0
      WRITE(6,9005)
    5 CALL FREAD (D,N,5,6)
      DO 10 I = 1,N
      IF(D(I) - 99999.) 6,11,6
    6 IF(D(I) - XMIN) 7,8,8
C   7 WRITE(6,9003) D(I)
    7 GO TO 10
    8 IF(D(I) - XMAX) 9,7,7
    9 J = (D(I) - XMIN)/CLINT + 1.
      F(J) = F(J) + 1
      S = S + D(I)
      S2 = S2 + D(I)**2
      ND = ND + 1
   10 CONTINUE
      GO TO 5
   11 XL = XMIN - CLINT
      WRITE(6,9008)
 9008 FORMAT(30X,'I----5---10---15---20---25---30---35---40---45---50')
      DO 13 I =  1,NINT
      XL = XL + CLINT
      XH = XL + CLINT - .0001
      CALL INIT (LINE,1,80,64)
      N =(100.*F(1))/ND + .5
      IF(N) 13,13,12
   12 IF(N - 80) 16,16,15
   15 N = 80
   16 CALL INIT (LINE,1,N,92)
   13 WRITE(6,9004) XL,XH,F(I),N,LINE
      WRITE(6,9008)
 9004 FORMAT(' ',2F10.4,I5,'(',I2,')I',20A4)
```

Computer Program (Continued)

```
 9005 FORMAT('0CLASS INTERVALS',6X,'FREQ(PCT)')
      AV = S/ND
      SD = SQRT((ND*S2 - S**2)/(ND*(ND - 1)))
      WRITE(6,9006) AV,SD,ND
 9006 FORMAT('0AVERAGE=',F15.4,', STD DEV =',F15.4,
     *', NUMBER OF OBSERVATIONS=',I5)
      GO TO 1
      END

CFTC LIST
      SUBROUTINE FREAD ( WEN, N, IREDT, IWRIT )
      DIMENSION NUM(80), IN(80), WEN(1)
  100 FORMAT (  80A1 )
  101 FORMAT (  ' INPUT IN ERROR--CHARACTER ENTERED IS NOT A NUMBER,'
     1 /, ' MINUS SIGN, PLUS SIGN, DECIMAL POINT, OR SPACE.' )
  103 FORMAT ( I3, ' NUMBERS WERE ASKED FOR.  YOU HAVE TYPED IN',
     1 I3, '.' )
  104 FORMAT ( ' PLEASE RETYPE ENTIRE LINE CORRECTLY.' )
  105 FORMAT ( ' INPUT IN ERROR--2 DECIMALS IN ONE NUMBER OR NO'
     1 ' SPACE BETWEEN NUMBERS.' )
   80 DO 200 J = 1, 80
  200 IN(J) = 0
      J=0
      KL=1
      JK=0
      NPT=0
      M=1
      SUNIM = 1.0
      LAST=0
      READ (IREDT,100)NUM
      I=0
   96 I=I+1
      IF(I - 81) 97,18,18
   97 IF ( NUM(I) - 1077952576 ) 99,13,99
   99 IF ( NUM(I) - 1799372864 ) 1,13,1
    1 IF ( NUM(I) - 1614823488 ) 3,2,3
    2 SUNIM= -1.0
      GO TO 96
    3 IF ( NUM(I) - 1312833600 ) 5,4,5
    4 SUNIM=1.0
      GO TO 96
    5 IF ( NUM(I) - 1262501952 ) 7,6,7
    6 NPT=NPT+1
      GO TO 96
    7 IF ( I-81 ) 8,18,18
    8 IN(M) = ( NUM(I) + 264224704 ) / 16777216
      IF ( IN(M) - 9 ) 9,9,20
    9 IF ( IN(M) ) 20,10,10
   10 IF ( NPT - 1 ) 11,12,19
   11 JK = JK + 1
```

Computer Program (Continued)

```
   12 M = M + 1
      GO TO 96
   13 IF ( KL - M ) 14,96,96
   14 NN = M
      J = J + 1
C     IF ( J - N ) 145,145,17
  145 WEN(J) = 0.0
      DO 15 K = KL,NN
      ADD = IN(K) * ( 10.0**(JK-1) )
      WEN(J) = WEN(J) + ADD
   15 JK = JK - 1
      WEN(J) = WEN(J) * SUNIM
      JK = 0
      KL = M
      NPT = 0
      SUNIM = 1.0
      IF ( LAST ) 96,96,21
   16 GO TO 96
   17 WRITE (IWRIT,103) N,J
      WRITE (IWRIT,104)
      GO TO 80
   18 LAST = 1
      IF(KL - M) 14,21,21
   19 WRITE (IWRIT,105)
      WRITE(IWRIT,104)
      GO TO 80
   20 WRITE (IWRIT,101)
      GO TO 80
   21 N = J
      RETURN
      END
/DATA

/END CARD READ, JOB TERMINATED

END OF JOB.
```

TYPICAL COMPUTER PRINTOUT

RUN NUMBER 2-81-1

CLASS INTERVALS		FREQ(PCT)
		I----5---10---15---20---25---30---35---40---45---50
0.0	0.9999	1(1)I*
1.0000	1.9999	2(2)I**
2.0000	2.9999	3(3)I***
3.0000	3.9999	23(23)I**********
4.0000	4.9999	38(38)I**********
5.0000	5.9999	21(21)I**********
6.0000	6.9999	8(8)I********
7.0000	7.9999	2(2)I**
8.0000	8.9999	2(2)I**
9.0000	9.9999	0(0)I
10.0000	10.9999	0(0)I
		I----5---10---15---20---25---30---35---40---45---50

AVERAGE = 4.1200 STANDARD DEVIATION = 1.3126 NUMBER OF OBSERVATIONS = 100

APPENDIX VI

COMPUTER PROGRAM FOR FINES-TO-FIBER INTERACTIONS

```
/ID 94000100
/FTC LIST
/JOB GO,TIME=10
BPS FORTRAN D COMPILER
 S.0001     10    READ(5,97)A1,A2,A3,A4,A5
 S.0002     97    FORMAT(5A4)
 S.0003           WRITE(6,96)A1,A2,A3,A4,A5
 S.0004     96    FORMAT('0',5A4)
 S.0005           READ(5,98)AWT,BWT,CWT,DWT,EWT,FWT
 S.0006           IF(AWT)100,100,1
 S.0007      1    READ(5,98)ACPM,BCPM,CCPM,DCPM,ECPM,FCPM
 S.0008           READ(5,98)DVOL,DVOLZ
 S.0009     98    FORMAT(8F10.1)
 S.0010           AVEC=(((ACPM-6.5)/AWT)+((BCPM-6.5)/BWT)+((CCPM-6.5)/CWT))/0.003
 S.0011           AVECZ=(((DCPM-6.5)/DWT)+((ECPM-6.5)/EWT)+((FCPM-6.5)/FWT))/0.003
 S.0012           AVCL=AVEC/DVOL
 S.0013           AVCLZ=AVECZ/DVOLZ
 S.0014           DOSEF=940334.0
 S.0015           PRET=((DOSEF-AVCL)*100.0)/DOSEF
 S.0016           DOSFZ=(DOSEF-(ACPM+BCPM+CCPM))/DVOLZ
 S.0017           AVALF=(1-(PRET*0.01))*DOSFZ
 S.0018           PRETZ=((AVALF-AVCLZ)*100.0)/AVALF
 S.0019           PRED=((DOSEF-AVCLZ)*100.0)/DOSEF
 S.0020           WRITE(6,91)
 S.0021     91    FORMAT(' ')
 S.0022           WRITE(6,99)AVCL,AVCLZ,PRET,PRETZ,PRED
 S.0023     99    FORMAT(1X,'AVCL,AVCLZ,PRET,PRETZ,PRED=',2E16.6,3F6.1)
 S.0024           GO TO 10
 S.0025    100    CALL EXIT
 S.0026           END
                     SIZE OF COMMON   00000    PROGRAM  01110
END OF COMPILATION  MAIN
/DATA


/END CARD READ, JOB TERMINATED


END OF JOB.
```

APPENDIX VII

ELECTROLYTE EFFECTS ON FIBER-TO-FIBER INTERACTIONS WITHOUT FINES

The data listed below are broken into four areas: A. no electrolyte, B. NaCl electrolyte, C. $CaCl_2$ electrolyte, and D. $LaCl_3$ electrolyte.

A. NO ELECTROLYTE

System Number	Degree of Fiber Coagulation, 255 rpm	Average
2-51-4	1.52	
2-54-1	1.51	
2-65-1	1.35	
2-66-2	1.70	
2-69-1	1.45	1.38 ± 0.18
2-71-1	1.10	± 13%
2-72-2	1.23	
2-75-1	1.35	
2-75-5	1.24	
	585 rpm	
2-57-1	0.09	
2-58-4	1.29	
2-60-1	1.12	
2-61-3	1.19	1.10 ± 0.21
2-67-4	1.09	± 11%
2-68-7	1.12	
2-73-1	0.97	
2-74-1	1.11	

B. SODIUM CHLORIDE ELECTROLYTE

System Number	Degree of Fiber Coagulation, 255 rpm	Average	Cation Concentration, M
2-52-1	1.31	1.52 ± 0.30	$1(10^{-4})$
2-54-2	1.73	± 20%	
2-52-2	1.40	1.49 ± 0.12	$1(10^{-3})$
2-54-3	1.57	± 8.6%	
2-52-3	1.66	1.79 ± 0.18	$5(10^{-3})$
2-54-4	1.91	± 10%	
2-52-4	1.72	1.94 ± 0.31	$1(10^{-2})$
2-55-1	2.16	± 16%	
2-52-5	1.72	1.90 ± 0.25	$5(10^{-2})$
2-55-2	2.07	± 13%	
2-53-1	1.65	1.78 ± 0.18	$1(10^{-1})$
2-55-3	1.90	± 11%	
	585 rpm		
2-57-2	1.17	1.16 ± 0.02	$1(10^{-4})$
2-60-2	1.14	± 1.7%	
2-57-3	1.10	1.17 ± 0.09	$1(10^{-3})$
2-59-2	1.23	± 7.7%	
2-57-4	1.36	1.47 ± 0.15	$5(10^{-3})$
2-59-3	1.57	± 10%	
2-58-1	1.37	1.44 ± 0.09	$1(10^{-2})$
2-59-3	1.50	± 6.2%	
2-58-3	1.62	1.47 ± 0.17	$1(10^{-1})$
2-59-6	1.60	± 12%	
2-63-1	1.41		
2-63-3	1.26		
2-61-2	1.40	1.50 ± 0.13	$5(10^{-1})$
2-61-6	1.59	± 8.7%	

C. CALCIUM CHLORIDE ELECTROLYTE

System Number	Degree of Fiber Coagulation, 255 rpm	Average	Cation Concentation, M
2-65-2	1.44	1.58 ± 0.18	$1(10^{-5})$
2-66-3	1.78	± 11%	
2-69-2	1.53		
2-65-3	1.42	1.52 ± 0.23	$5(10^{-5})$
2-66-4	1.26	± 15%	
2-69-3	1.78		
2-65-4	1.36	1.54 ± 0.16	$1(10^{-4})$
2-66-5	1.66	± 10%	
2-69-4	1.61		
2-65-5	1.52	1.77 ± 0.188	$5(10^{-4})$
2-67-1	1.96	± 10%	
2-69-5	1.83		
2-65-6	1.58	1.80 ± 0.19	$1(10^{-3})$
2-67-2	1.94	± 11%	
2-69-6	1.87		
2-66-1	1.70	1.72 ± 0.03	$5(10^{-3})$
2-69-7	1.74	± 1.7%	
	585 rpm		
2-68-1	1.18	1.22 ± 0.05	$1(10^{-5})$
2-68-7	1.26	± 4.9%	
2-68-2	1.18	1.17 ± 0.01	$5(10^{-5})$
2-68-9	1.16	± 0.85%	
2-68-3	1.25	1.23 ± 0.04	$1(10^{-4})$
2-68-10	1.20	± 3.2%	
2-68-4	1.42	1.33 ± 0.16	$5(10^{-4})$
2-68-11	1.24	± 12%	
2-68-5	1.60	1.49 ± 0.16	$1(10^{-3})$
2-68-12	1.38	± 11%	
2-68-6	1.54	1.46 ± 0.11	$5(10^{-3})$
2-68-13	1.38	± 7.5%	

D. LANTHANUM CHLORIDE ELECTROLYTE

System Number	Degree of Fiber Coagulation, 255 rpm	Average	Cation Concentration, M
2-71-2	1.36	1.42 ± 0.08	$1(10^{-6})$
2-72-3	1.47	± 5.6%	
2-71-3	1.28	1.32 ± 0.06	$5(10^{-6})$
2-72-4	1.36	± 4.5%	
2-71-4	1.39	1.40 ± 0.01	$1(10^{-5})$
2-72-5	1.41	± 0.72%	
2-71-5	1.93	1.78 ± 0.22	$5(10^{-5})$
2-72-6	1.62	± 12%	
2-71-6	2.06	1.90 ± 0.23	$1(10^{-4})$
2-72-7	1.73	± 12%	
2-72-1	1.97	1.89 ± 0.11	$5(10^{-4})$
2-72-8	1.81	± 5.8%	
	585 rpm		
2-73-2	1.26	1.16 ± 0.14	$1(10^{-6})$
2-74-2	1.05	± 12%	
2-73-3	1.11	1.19 ± 0.11	$5(10^{-6})$
2-74-3	1.26	± 9.1%	
2-73-4	1.50	1.55 ± 0.07	$1(10^{-5})$
2-74-4	1.60	± 4.5%	
2-73-5	1.46	1.55 ± 0.16	$5(10^{-5})$
2-74-5	1.63	± 10%	
2-73-6	1.53	1.46 ± 0.11	$1(10^{-4})$
2-74-6	1.38	± 7.5%	
2-73-7	1.56	1.53 ± 0.04	$5(10^{-4})$
2-74-7	1.50	± 2.6%	

APPENDIX VIII

POLYMER EFFECTS ON FIBER-TO-FIBER INTERACTIONS WITHOUT FINES

The data listed in this appendix are broken first into cationic, anionic, and nonionic systems. Each system is divided into agitation and pH sections.

CATIONIC POLYMER

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation	Average
A. pH 7; 255 RPM			
2-15-1	0.0	1.37	1.41 ± 0.14
2-17-1		1.37	± 9.9%
2-19-1		1.58	
2-29-1		1.50	
2-30-8		1.46	
2-01-1		1.31	
2-07-1		1.65	
2-97-3		1.24	
2-100-1		1.26	
2-15-2	10.0	1.80	1.57 ± 0.14
2-15-3		1.39	± 8.9%
2-30-1		1.49	
2-30-2		1.57	
2-07-2		1.66	
2-97-4		1.53	
2-15-4	20.0	2.52	1.98 ± 0.33
2-16-1		2.21	± 17%
2-82-4		2.09	
2-97-5		1.59	
2-100-2[a]		2.01	
2-98-3[a]		1.61	
2-100-3		1.85	
2-16-2	30.0	2.02	1.93 ± 0.27
2-16-3		2.05	± 14%
2-97-6[a]		1.79	
2-98-4		1.67	
2-100-4		2.36	
2-100-5		1.68	

See p. 166 for footnote.

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation	Average
2-16-4	40.0	1.66	2.03 ± 0.27
2-16-5		1.88	± 13%
2-100-6		2.03	
2-100-7		2.33	
2-98-5		2.24	
2-98-2	50.0	1.86	2.10 ± 0.17
2-98-6		2.07	± 8.1%
2-100-8		2.23	
2-100-9		2.22	
3-1-1	60.0	1.42	1.66 ± 0.53
3-1-2		1.89	± 20%
B. pH 5; 255 RPM			
2-84-1	0.0	1.38	1.40 ± 0.13
2-85-5		1.29	± 9.3%
2-90-1		1.54	
2-84-2	10.0	2.83	1.68 ± 0.21
2-86-3		1.53	± 13%
2-85-6	20.0	1.85	1.83 ± 0.03
2-86-5		1.80	± 1.6%
2-84-3	30.0	1.86	1.87 ± 0.01
2-88-6		1.87	± 0.5%
2-90-2	40.0	2.52	2.28 ± 0.35
2-90-4		2.03	± 15%
2-92-1	50.0	1.91	1.82 ± 0.13
2-92-2		1.73	± 7.1%
C. pH 9; 255 RPM			
2-85-1	0.0	1.37	1.51 ± 0.16
2-85-3[a]		1.73	± 11%
2-86-1[a]		1.45	
2-88-4		1.70	
3-14-2		1.36	
3-18-1		1.44	
2-86-4	10.0	1.45	1.61 ± 0.22
2-88-1		1.76	± 14%
2-85-4	20.0	1.68	1.69 ± 0.01
2-86-6[a]		1.69	± 0.6%

See p. 166 for footnote.

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation	Average
2-88-3	30.0	1.73	2.00 ± 0.37
2-88-5		2.26	± 18%
2-90-5[a]	40.0	2.08	2.01 ± 0.11
2-90-6		1.93	± 5.5%
2-92-3	50.0	1.65	1.78 ± 0.18
2-92-4		1.90	± 10%
A. pH 7; 585 RPM			
2-17-2	0.0	1.25	1.21 ± 0.08
2-17-3		1.17	± 6.3%
2-21-1		1.16	
2-23-1		1.33	
2-31-5		1.16	
2-17-4	10.0	1.96	1.91 ± 0.08
2-17-5		1.85	± 5.0%
2-17-6	20.0	1.04	1.05 ± 0.16
2-18-1		1.27	± 15%
2-30-3		1.01	
2-30-4		0.88	
2-18-2	30.0	0.97	0.84 ± 0.10
2-18-3		0.78	± 12%
2-30-6		0.87	
2-30-7		0.74	
2-18-4	40.0	0.78	0.71 ± 0.10
2-30-5		0.64	± 14%
B. pH 5; 585 RPM			
2-93-1	0.0	1.12	0.99 ± 0.13
2-94-3		1.04	± 13%
3-05-1		0.98	
3-07-1		0.81	
2-96-1	10.0	1.74	1.78 ± 0.06
2-96-3		1.82	± 3.4%
2-93-2	20.0	1.22	1.19 ± 0.04
2-94-4		1.16	± 3.4%
2-93-3	30.0	0.87	0.85 ± 0.03
2-94-5		0.84	± 3.5%

See p. 166 for footnote.

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation	Average
2-93-4	40.0	0.75	0.76 ± 0.01
2-94-6		0.77	± 1.3%
C. pH 9; 585 RPM			
2-93-5	0.0	0.96	0.98 ± 0.17%
2-94-7		1.17	± 17%
3-9-1		1.01	
3-10-1		0.78	
2-96-2	10.0	1.66	1.81 ± 0.21
2-96-4		1.95	± 12%
2-93-6	20.0	1.12	1.19 ± 0.10
2-94-8		1.26	± 8.4%
2-94-1	30.0	1.05	0.94 ± 0.16
2-95-1		0.83	± 17%
2-94-2	40.0	0.67	0.75 ± 0.11
2-95-2		0.82	± 15%
ANIONIC POLYMER			
A. pH 7; 255 RPM			
3-20-2	0.0	1.09	1.20 ± 0.07
3-20-4		1.19	± 5.4%
3-26-4		1.26	
3-32-1		1.17	
3-32-5		1.12	
3-33-6		1.29	
3-35-2		1.22	
3-43-4		1.25	
3-45-1		1.21	
3-56-2	10.0	1.23	1.36 ± 0.18
3-46-4		1.48	± 13%
3-46-1	20.0	1.59	1.56 ± 0.05
3-46-5		1.52	± 3.2%
3-47-4	30.0	1.45	1.51 ± 0.08
3-46-6		1.57	
3-43-5	40.0	1.44	1.42 ± 0.12
3-43-6		1.24	± 8.7%
3-49-1		1.53	
3-49-2		1.45	

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation	Average
3-47-2	50.0	1.08	1.09 ± 0.01
3-47-3		1.09	± 1.3%
B. pH 5; 255 RPM			
3-41-4	0.0	1.26	1.24 ± 0.04
3-43-1		1.21	± 2.3%
3-40-4	10.0	1.69	1.64 ± 0.07
3-40-8		1.59	± 4.3%
3-40-5	20.0	1.77	1.71 ± 0.09
3-41-1		1.64	± 5.4%
3-40-6	30.0	1.59	1.63 ± 0.06
3-41-2		1.67	± 3.5%
3-40-7	40.0	1.39	1.47 ± 0.11
3-41-3		1.55	± 7.7%
3-49-3	50.0	1.29	1.30 ± 0.01
3-49-4		1.41	± 0.8%
C. pH 9; 255 RPM			
3-38-1	0.0	1.37	1.29 ± 0.07
3-40-1		1.25	± 5.4%
3-47-1		1.24	
3-40-2	10.0	1.48	1.50 ± 0.02
3-40-2		1.51	± 1.4%
3-38-2	20.0	1.70	1.73 ± 0.03
3-48-1		1.70	± 1.7%
3-48-2		1.70	
3-47-5	30.0	1.88	1.77 ± 0.16
3-47-6		1.66	± 8.8%
3-39-1	40.0	1.53	1.42 ± 0.15
3-39-5		1.32	± 10%
3-39-2	50.0	1.26	1.41 ± 0.21
3-39-6		1.56	± 15%

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation	Average
A. pH 7; 585 RPM			
See Cationic 585 rpm	0.0		1.21 ± 0.08 ± 6.3%
2-21-2	10.0	0.96	0.96 ± 0.0
2-21-3		0.96	± 0.0%
2-21-4	20.0	0.92	0.94 ± 0.02
2-21-5		0.96	± 3.2%
2-21-6	30.0	1.23	1.3 ± 0.11
2-21-7		1.39	± 8.4%
2-22-1	40.0	1.00	1.05 ± 0.06
2-22-2		1.09	± 5.7%
2-31-3	50.0	0.73	0.74 ± 0.01
2-31-4		0.74	± 1.4%
B. pH 5; 585 RPM			
See Cationic 585 rpm	0.0		0.99 ± 0.13 ± 13%
3-5-2	10.0	1.09	0.88 ± 0.21
3-5-3		0.68	± 23%
3-7-2		0.87	
3-6-1	20.0	0.84	1.04 ± 0.24
3-6-2		1.28	± 23%
3-7-3		1.00	
3-6-3[a]	30.0	0.91	1.05 ± 0.20
3-6-4		1.19	± 19%
3-6-5	40.0	1.04	1.01 ± 0.04
3-6-6		0.98	± 4.0%
3-6-7[a]	50.0	0.97	0.96 ± 0.02
3-6-8		0.94	± 2.1%
C. pH 9; 585 RPM			
See Cationic 585 rpm	0.0		0.98 ± 0.17 ± 17%

See p. 166 for footnote.

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation	Average
3-8-1	10.0	0.81	0.87 ± 0.08
3-8-2		0.93	± 9.2%
3-8-3	20.0	0.93	0.90 ± 0.05
3-8-4[a]		0.86	± 5.6%
3-8-5	30.0	0.75	0.87 ± 0.17
3-8-6		0.99	± 19%
3-8-7	40.0	0.72	0.77 ± 0.07
3-8-8		0.82	± 9.1%
3-8-9	50.0	0.74	0.78 ± 0.06
3-8-10		0.82	± 7.7%

NONIONIC POLYMER

A. pH 7; 255 RPM

See Anionic 255 rpm	0.0		1.20 ± 0.07
3-49-5	10.0	1.35	1.34 ± 0.02
2-50-4		1.32	± 1.6%
3-50-1	20.0	1.30	1.28 ± 0.03
3-50-5		1.26	± 2.3%
3-50-2	30.0	1.37	1.37 ± 0.0
3-50-6		1.37	± 0.0%
3-43-5	40.0	1.44	1.34 ± 0.14
3-43-6		1.24	± 10.6%
3-50-3	50.0	1.23	1.20 ± 0.05
3-50-7		1.16	± 4.1%

B. pH 5; 255 RPM

See Anionic 255 rpm	0.0		1.24 ± 0.04 ± 2.3%
3-41-5	10.0	1.35	1.30 ± 0.08
3-42-4		1.24	± 6.0%
3-42-5	20.0	1.52	1.42 ± 0.09
3-43-2		1.40	± 6.5%
3-43-3		1.34	

See p. 166 for footnote.

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation	Average
3-42-2	30.0	1.43	1.27 ± 0.23
3-42-6		1.10	± 18%
3-42-3	40.0	1.47	1.39 ± 0.12
3-42-7		1.30	± 8.6%
3-56-1	50.0	1.09	1.07 ± 0.04
3-56-2		1.04	± 3.3%
C. pH 9; 255 RPM			
See Anionic 255 rpm	0.0		1.29 ± 0.07
			± 5.4%
3-51-1	10.0	1.36	1.32 ± 0.06
3-51-6		1.28	± 4.3%
3-51-2	20.0	1.42	1.46 ± 0.05
3-51-7		1.49	± 3.4%
3-51-3	30.0	1.42	1.48 ± 0.08
3-52-1		1.53	± 5.3%
3-51-4	40.0	1.34	1.30 ± 0.06
3-52-2		1.26	± 4.4%
3-51-5	50.0	1.23	1.25 ± 0.03
3-52-3		1.27	± 2.3%
A. pH 7; 585 RPM			
See Cationic 585 rpm	0.0		1.21 ± 0.08
			± 6.3%
2-25-2	10.0	0.99	0.94 ± 0.08
2-25-5		0.88	± 8.5%
2-25-3	20.0	1.04	1.11 ± 0.09
2-25-4		1.17	± 8.1%
2-25-6	30.0	1.09	1.07 ± 0.03
2-25-7		1.05	± 2.8%
2-25-8	40.0	1.22	1.14 ± 0.21
2-25-9		1.06	± 10%

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation	Average
B. pH 5; 585 RPM			
See Cationic 585 rpm	0.0		0.99 ± 0.13 ± 13%
3-18-5	10.0	0.92	0.82 ± 0.15
3-18-6		0.71	± 18%
3-18-7	20.0	0.69	0.73 ± 0.06
3-18-8		0.77	± 8.2%
3-19-1[a]	30.0	0.74	0.74 ± 0.0
3-19-2		0.74	± 0.0%
3-19-3	40.0	0.70	0.71 ± 0.01
3-19-4		0.72	± 1.4%
C. pH 9; 585 RPM			
See Cationic 585 rpm	0.0		0.98 ± 0.17 ± 17%
3-09-2	10.0	1.12	1.09 ± 0.04
3-10-2		1.06	± 3.7%
3-10-3	20.0	0.77	0.74 ± 0.05
3-10-4		0.70	± 6.8%
3-14-1	30.0	1.05	0.94 ± 0.16
3-10-5		0.82	± 17%
3-10-7	40.0	0.99	0.91 ± 0.11
3-10-8		0.83	± 12%

[a]Calculated with a raw data point omitted which was out of line with the rest of the data points.

The data presented below are for the 585 rpm anionic system retrial with batch II fiber.

ANIONIC POLYMER RETRIAL

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation	Average
A. pH 7; 585 RPM			
3-36-1	0.0	0.36	0.41 ± 0.06
3-37-1		0.45	± 16%
3-36-2	30.0	0.56	0.57 ± 0.01
3-37-2		0.58	± 2.5%
3-36-3	50.0	0.50	0.55 ± 0.07
3-37-3		0.60	± 13%

APPENDIX IX

POLYMER PLUS $LaCl_3$ ELECTROLYTE EFFECTS ON FIBER-TO-FIBER INTERACTIONS WITHOUT FINES

The data presented in this appendix are divided into cationic, anionic, and nonionic polymer sections. Each section includes both the agitation and pH divisions. A separate section presented first will present data without $LaCl_3$ or polymer additives. All polymer sections are with $LaCl_3$ present. Since, no difference in pH was found, the no additive value will be reported as only one value.

NO ADDITIVES

System Number	Degree of Fiber Cluster Formation	Average
	255 rpm	
3-20-2	1.09	1.22 ± 0.07
3-20-4	1.19	± 5.7%
3-26-4	1.26	
3-32-1	1.17	
3-32-5	1.12	
3-33-6	1.29	
3-35-2	1.22	
3-43-4	1.25	
3-45-1	1.21	
3-41-4	1.26	
3-43-1	1.21	
3-38-1	1.37	
3-40-1	1.25	
3-47-1	1.24	
	585 rpm	
3-20-3	0.41	0.44 ± 0.08
3-21-1	0.50	± 18%
3-24-1	0.46	
3-27-1	0.38	
3-20-1	0.55	
3-30-1	0.33	
3-30-4	0.45	

CATIONIC POLYMER

System Number	Polymer Concentration, ppm	Degree of Fiber Cluster Formation	Average
A. pH 7; 255 RPM			
3-57-1	0.0	1.51	1.54 ± 0.04
3-58-4		1.56	± 2.3%
3-60-1	2.0	1.76	1.71 ± 0.08
3-60-5		1.65	± 4.5%
3-60-2	4.0	1.32	1.38 ± 0.08
3-61-1		1.44	± 6.1%
3-60-3	6.0	1.28	1.33 ± 0.06
3-61-2		1.37	± 4.8%
3-60-4	8.0	1.34	1.30 ± 0.06
3-61-3		1.25	± 4.9%
3-57-2	10.0	1.02	1.14 ± 0.17
3-58-5		1.26	± 14.9%
B. pH 5; 255 RPM			
3-59-2	0.0	1.68	1.73 ± 0.06
3-59-4[a]		1.77	± 3.7%
3-91-1	0.5	1.91	1.89 ± 0.03
3-91-2		1.87	± 1.5%
3-91-3	1.0	2.21	2.23 ± 0.02
3-91-4		2.24	± 1.0%
3-61-4	2.0	1.57	1.51 ± 0.09
3-61-8		1.44	± 6.1%
3-61-5	4.0	1.48	1.44 ± 0.06
3-62-1		1.39	± 4.4%
3-61-6	6.0	1.55	1.51 ± 0.06
3-62-2		1.46	± 4.2%
3-61-7	8.0	1.44	1.38 ± 0.08
3-62-3		1.32	± 6.1%
3-59-3	10.0	1.26	1.41 ± 0.21
3-59-5		1.56	± 15%

See p. 175 for footnote.

System Number	Polymer Concentration, ppm	Degree of Fiber Cluster Formation	Average
C. pH 9; 255 RPM			
3-63-1	0.0	1.69	1.70 ± 0.01
3-63-3		1.70	± 0.4%
3-91-1	0.5	1.91	1.89 ± 0.03
3-91-2		1.87	± 1.5%
3-91-3	1.0	2.21	2.23 ± 0.02
3-91-4		2.24	± 1.0%
3-64-3	2.0	1.63	1.63 ± 0.01
3-64-7		1.62	± 0.4%
3-64-4	4.0	1.64	1.58 ± 0.08
3-64-8		1.52	± 5.4%
3-64-5	6.0	1.23	1.34 ± 0.15
3-64-9		1.44	± 11%
3-64-6	8.0	1.37	1.40 ± 0.04
3-64-10		1.42	± 2.5%
3-63-2	10.0	1.31	1.29 ± 0.03
3-63-4		1.27	± 2.2%
A. pH 5; 585 RPM			
3-75-1	0.0	0.52	0.53 ± 0.01
3-77-1		0.52	± 2.3%
3-78-1		0.54	
3-75-3	2.0	0.63	0.66 ± 0.04
3-80-1		0.69	± 6.4%
3-75-4	4.0	0.59	0.62 ± 0.04
3-80-2		0.64	± 5.7%
3-75-5	6.0	0.50	0.55 ± 0.06
3-80-3		0.59	± 11.6%
3-75-6	8.0	0.53	0.50 ± 0.04
3-80-4		0.47	± 8.5%

System Number	Polymer Concentration, ppm	Degree of Fiber Cluster Formation	Average
B. pH 9; 585 RPM			
3-82-1	0.0	0.52	0.52 ± 0.04
3-83-5		0.49	± 6.8%
3-85-1		0.56	
3-80-6	2.0	0.72	0.74 ± 0.02
3-81-3		0.75	± 2.4%
3-80-7	4.0	0.64	0.68 ± 0.05
3-81-4		0.71	± 7.3%
3-80-8	6.0	0.52	0.52 ± 0.01
3-81-5		0.51	± 1.4%
3-81-1	8.0	0.53	0.51 ± 0.03
3-81-6		0.49	± 5.5%
3-81-2	10.0	0.54	0.48 ± 0.09
3-81-7		0.41	± 19%
ANIONIC POLYMER			
A. pH 5; 255 RPM			
3-59-2	0.0	1.68	1.69 ± 0.08
3-59-4[a]		1.77	± 4.5%
3-65-1		1.62	
3-65-3	2.0	1.93	1.73 ± 0.28
3-66-4		1.53	± 16%
3-66-1	4.0	1.86	1.94 ± 0.11
3-66-5		2.02	± 5.8%
3-66-2	6.0	1.80	1.77 ± 0.04
3-66-6		1.74	± 2.4%
3-66-3	8.0	1.86	1.96 ± 0.13
3-66-7		2.05	± 6.9%
3-65-2	10.0	1.57	1.52 ± 0.08
3-66-8		1.46	± 5.1%
3-69-2	20.0	1.15	1.13 ± 0.03
3-69-4		1.11	± 2.5%

See p. 175 for footnote.

System Number	Polymer Concentration, ppm	Degree of Fiber Cluster Formation	Average
B. pH 9; 255 RPM			
3-63-1 3-63-3	0.0	1.69 1.70	1.70 ± 0.01 ± 0.4%
3-67-2 3-67-6	2.0	1.78 1.39	1.59 ± 0.28 ± 17%
3-67-3 3-67-7	4.0	1.87 2.00	1.94 ± 0.09 ± 4.7%
3-67-4 3-67-8	6.0	1.99 1.98	1.99 ± 0.01 ± 0.4%
3-67-5 3-67-9	8.0	2.35 2.16	1.16 ± 0.13 ± 6.0%
3-67-1 3-67-10	10.0	1.55 1.63	1.59 ± 0.06 ± 3.6%
A. pH 5; 585 RPM			
See Cationic 585 rpm	0.0		0.53 ± 0.01 ± 2.3%
3-77-3 3-84-1	2.0	0.46 0.55	0.51 ± 0.06 ± 13%
3-77-4 3-84-2	4.0	0.47 0.54	0.51 ± 0.05 ± 9.7%
3-77-5 3-84-3	6.0	0.45 0.50	0.48 ± 0.04 ± 7.4%
3-77-6 3-84-4	8.0	0.58 0.53	0.56 ± 0.04 ± 6.3%
3-77-2 3-84-5	10.0	0.53 0.54	0.54 ± 0.01 ± 1.3%
3-77-7	20.0	0.59	0.59
B. pH 9; 585 RPM			
See Cationic 585 rpm	0.0		0.52 ± 0.04 ± 6.8%

System Number	Polymer Concentration, ppm	Degree of Fiber Cluster Formation	Average
3-83-1	2.0	0.56	0.52 ± 0.06
3-83-7		0.48	± 10.9%
3-83-2	4.0	0.46	0.53 ± 0.09
3-83-8		0.59	± 17.3%
3-83-3	6.0	0.54	0.53 ± 0.01
3-83-9		0.52	± 2.7%
3-83-4	8.0	0.51	0.49 ± 0.04
3-83-10		0.46	± 7.2%
3-82-2	10.0	0.43	0.52 ± 0.05
3-83-6		0.55	± 9.5%
4-74-3	20.0	0.56	0.56

NONIONIC POLYMER

A. pH 5; 255 RPM

3-59-2	0.0	1.63	1.67 ± 0.07
3-59-4[a]		1.77	± 4.4%
3-65-1		1.62	
3-69-5		1.61	
3-70-1	4.0	1.86	1.86
3-70-2	6.0	1.65	1.65
3-70-3	8.0	2.15	2.15
3-69-6	10.0	1.83	1.97 ± 0.19
3-71-1		2.11	± 10%
3-70-4	20.0	1.84	1.92 ± 0.11
3-71-2		2.00	± 5.9%
3-70-5	30.0	1.95	1.96 ± 0.01
3-71-2		1.97	± 0.7%
3-70-6	40.0	2.24	2.13 ± 0.16
3-71-4		2.02	± 7.3%
3-72-1	50.0	1.75	1.73 ± 0.03
3-72-3		1.71	± 1.6%
3-72-2	60.0	1.77	1.66 ± 0.16
3-72-4		1.54	± 9.8%

See p. 175 for footnote.

System Number	Polymer Concentration, ppm	Degree of Fiber Cluster Formation	Average
B. pH 9; 255 RPM			
3-63-1	0.0	1.69	1.66 ± 0.04
3-63-3		1.70	± 2.5%
3-73-1		1.65	
3-73-3		1.61	
3-73-2	10.0	1.82	1.87 ± 0.06
3-73-4		1.91	± 3.4%
3-73-5	20.0	1.95	1.96 ± 0.01
3-73-6		1.96	± 0.5%
3-73-7	30.0	1.93	2.02 ± 0.12
3-73-8		2.10	± 6.0%
3-74-1	40.0	2.03	1.95 ± 0.11
3-74-2		1.87	± 5.8%
3-74-3	50.0	1.60	1.67 ± 0.10
3-74-4		1.74	± 5.9%
3-74-5	60.0	1.63	1.66 ± 0.04
3-74-6		1.69	± 2.6%
A. pH 5; 585 RPM			
See Cationic 585 RPM	0.0		0.53 ± 0.01
			± 2.3%
3-78-3	2.0	0.46	0.48 ± 0.03
3-85-3		0.50	± 5.9%
3-78-4	4.0	0.55	0.55 ± 0.01
3-85-4		0.54	± 2.6%
3-78-5	6.0	0.49	0.53 ± 0.05
3-86-1		0.56	± 9.3%
3-78-6	8.0	0.53	0.51 ± 0.03
3-86-2		0.49	± 5.5%
3-78-2	10.0	0.51	0.53 ± 0.03
3-87-3		0.55	± 5.3%
3-78-7	20.0	0.54	0.54
3-78-8	30.0	0.51	0.51
3-78-9	40.0	0.52	0.52

System Number	Polymer Concentration, ppm	Degree of Fiber Cluster Formation	Average
B. pH 9; 585 RPM			
See Cationic 585 rpm	0.0		0.52 ± 0.04 ± 6.8%
3-86-3	2.0	0.52	0.51 ± 0.01
3-86-4		0.50	± 6.8%
3-86-5	4.0	0.48	0.50 ± 0.03
3-86-6		0.52	± 5.7%
3-86-7	6.0	0.58	0.55 ± 0.05
3-86-8		0.51	± 9.0%
3-86-9	8.0	0.56	0.53 ± 0.04
3-87-1		0.50	± 8.0%
3-85-2	10.0	0.51	0.52 ± 0.01
3-87-2		0.52	± 1.4%

[a] Calculated without one data point which was out of line with the rest of the points.

APPENDIX X

DETERMINATION OF FIBER CONSISTENCY

Three separate fiber consistencies were evaluated in order to determine the consistency to be used in the current study. The consistencies evaluated included 0.1, 0.5, and 1.0% of oven-dried fiber per 100 grams of total slurry weight. Null indicator for the 0.1% system ranged from -2 to +1, indicating that there was not sufficient light reflected for enough experimental sensitivity. Ten evaluations were made on each fiber consistency, with each evaluation composed of 300 data points taken from the null indicator meter. A new sample of test pulp was used for each individual evaluation. For the 0.5% consistency, it was found that the reproducibility via a standard deviation calculation was precise to 3.9% when all 300 data points were used and to 7.4% when only the first 100 data points were used. For the 1.0% consistency, it was found that system reproducibility was precise to 10.0% when only the first 100 data points were used. The system evaluations for the 0.5 and 1.0% consistency runs are presented in Table XVII. From the data in Table XVII, it is seen that the precision was better for the 0.5% system than for the 1.0% system. This result does not mean that another consistency would not perform better, but since the 0.5% consistency is within the error limits expected from random sampling of 100 and 300 points, the 0.5% consistency figure was chosen to be used throughout the experimental program.

TABLE XVII

EXPERIMENTAL DETERMINATION OF FIBER CONSISTENCY

System Number	Degree of Fiber Cluster Formation	Average
	300 Point Runs at 0.5% Consistency	
1-48-1	6.08	6.23 ± 0.24
1-48-2	5.87	± 3.90%
1-48-3	6.02	
1-49-1	6.33	
1-50-2	6.00	
1-51-3	6.55	
1-51-4	6.52	
1-52-1	6.11	
1-53-1	6.47	
1-51-2	6.36	
	100 Point Runs at 0.5% Consistency	
1-48-1A	6.69	6.08 ± 0.45
1-48-2A	5.42	± 7.4%
1-48-3A	5.76	
1-49-1A	5.64	
1-50-2A	5.93	
1-51-3A	6.74	
1-51-4A	6.06	
1-52-1A	6.31	
1-53-1A	5.79	
1-51-2A	6.46	
	300 Point Runs at 1.0% Consistency	
1-59-4	9.65	10.50 ± 1.12
1-60-1	9.63	± 10%
1-60-4	12.49	
1-61-1	9.85	
1-61-2	9.50	
1-61-3	10.69	
1-61-4	9.51	
1-62-1	10.49	
1-62-2	10.91	
1-62-3	12.27	
	100 Point Runs at 1.0% Consistency	
1-59-4A	8.89	10.40 ± 1.57
1-60-1A	9.63	± 15%
1-60-4A	12.13	
1-61-1A	9.25	
1-61-2A	8.19	
1-61-3A	11.55	
1-61-4A	9.53	
1-62-1A	10.58	
1-62-2A	13.12	
1-62-3A	11.15	

APPENDIX XI

IMPELLER POSITION

Chiu (39) has noted that the degree of fiber cluster formation is dependent on the geometry of the impeller system. A study was conducted on the present test system to establish the optimum impeller arrangement. Angles of entry into the slurry of 85.0, 72.5, and 69.5° were evaluated. The measured angle was actually the complimentary angle to the angle at which the impeller entered the slurry. The measured angle is depicted in Fig. 31. The results of the fiber cluster formation determinations for the three angles in question are presented in Table XVIII. All evaluations in Table XVIII were carried out at 300 rpm and at pH 7.0. Note that the degree of fiber cluster formation does depend on the impeller positioning, with reproducibility decreasing and system sensitivity increasing as the impeller entrance angle decreased. The 72.5° test angle was selected for all experimental evaluations, losing some in system reproducibility while gaining some in system sensitivity.

TABLE XVIII

DETERMINATION OF IMPELLER ANGLE

System Number	Impeller Entrance Angle	Degree of Fiber Cluster Formation	Average
1-82-1A	75.0	2.31	2.42 ± 0.16
1-82-2A		2.53	± 6.2%
1-82-3A	72.5	3.73	4.14 ± 0.57
1-83-1A		4.54	± 12%
1-83-2A	69.5	7.44	6.65 ± 1.12
1-83-3A		5.86	± 14%

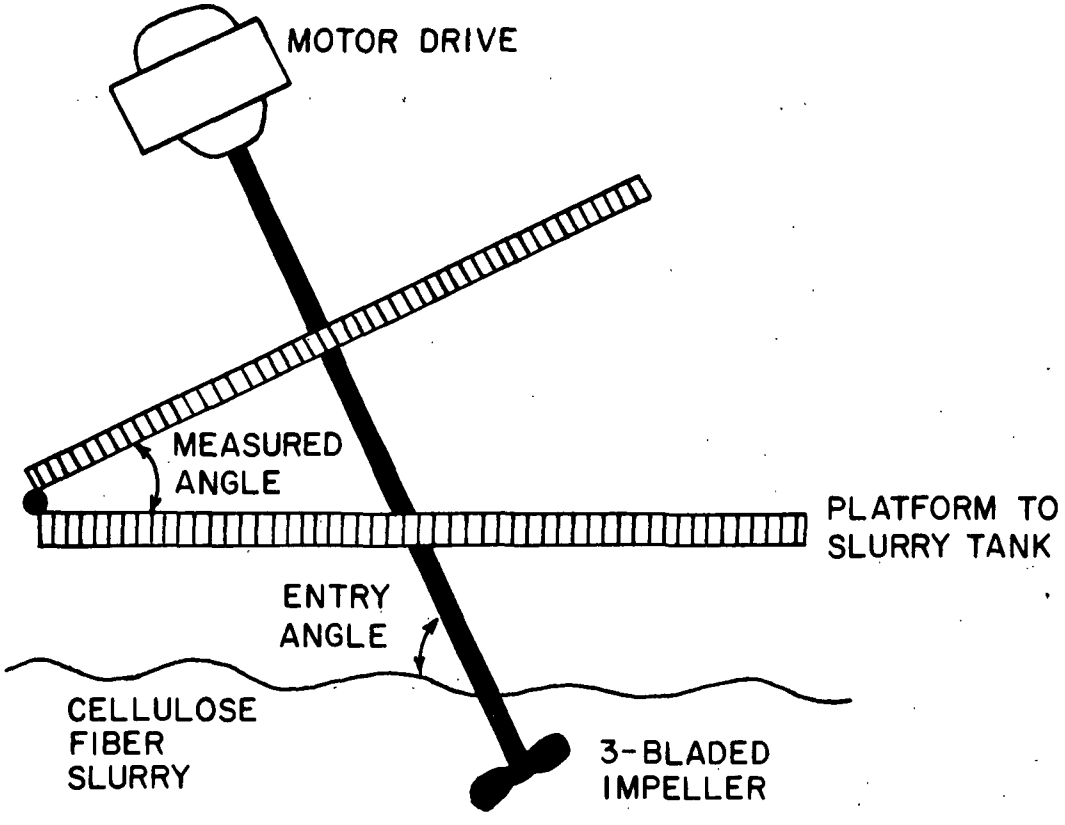


Figure 31. Angle of Impeller Entry into Cellulose Fiber Slurry

APPENDIX XII

SYSTEM REPRODUCIBILITY

System Number	Degree of Fiber Cluster Formation	Average
1-48-1	6.69	6.08 ± 0.44
1-48-2	5.42	± 7.2%
1-48-3	5.76	
1-49-1	5.64	
1-50-2	5.93	
1-51-2	6.74	
1-51-3	6.06	
1-51-4	6.31	
1-52-1	5.79	
1-53-1	6.46	

The test runs given above are for pH 7 at 300 rpm without additives. The first column of standard deviations was determined on the basis of the 100 experimental data points. The 0.44 is the standard deviation of the 10 standard deviations listed.

APPENDIX XIII

CUTTING ACTION INFLUENCE OF IMPELLER BLADES

The data presented in this appendix are for a six-bladed impeller of the same size and shape as the three-bladed impeller. Evaluations were conducted at 255 and 585 rpm for pH 7.0 with the cationic polymer. Results shown in Table XIX should be compared with the results presented in Fig. 11 and Appendix VIII. Note that the percentage changes from the maximum degree of fiber cluster formation to the zero polymer point are very nearly the same: 32 and 33% at 255 rpm for the three and six-bladed impeller, respectively; while 40 and 45% at 585 rpm for the three and six-bladed impeller, respectively. Polymer concentrations where the maximum degree of fiber flocculation occurs were the same for the three and six-bladed impellers.

TABLE XIX

CUTTING EFFECTS OF IMPELLER ON FIBER FLOCCULATION

System Number	Polymer Concentration	Degree of Fiber Flocculation
	255 rpm	
4-55-1	0.0	0.41
4-55-2	10.0	0.75
4-55-3	20.0	0.52
4-55-4	30.0	0.44
4-56-1	40.0	0.37
	585 rpm	
4-56-2	0.0	1.20
4-56-3	20.0	1.34
4-56-4	30.0	1.55
4-56-5	40.0	1.79
4-56-6	50.0	1.50
4-56-7	60.0	1.36

APPENDIX XIV

EFFECTS OF AGITATION TIME ON FIBER CLUSTER FORMATION

The first series of data are for the effects of extended periods of agitation of fiber-to-fiber interactions without the influence of additives. Systems were checked at pH 7.0 and both 255 and 585 rpm. These results, presented in Table XX, indicated that over a 23-hour period without additives, the degree of fiber cluster formation was not affected.

TABLE XX

TIME OF AGITATION DATA ON FIBER-TO-FIBER INTERACTIONS WITHOUT ADDITIVES

System Number	Degree of Fiber Cluster Formation	Time of Agitation, hr
	255 rpm	
1-80-1	3.56	0.0
1-80-2	4.08	0.5
1-80-3	3.53	1.5
1-80-4	4.22	2.5
1-81-1	3.47	5.5
1-81-2	3.63	9.5
1-81-3	3.67	14.0
1-81-4	4.21	23.5
	585 rpm	
1-73-6	2.14	0.0
1-74-1	2.31	0.5
1-74-2	2.44	1.5
1-74-3	2.42	2.5
1-74-4	2.30	5.5
1-74-5	2.88	9.5
1-74-6	2.46	13.5
1-74-7	2.46	23.0

The results presented in Table XXI are for the three test polymer systems evaluated for at least 30 minutes of agitation at 585 rpm both with

and without $LaCl_3$. These results also indicated no effect on the degree of fiber cluster formation on extended periods of agitation.

TABLE XXI

TIME OF AGITATION DATA ON FIBER-TO-FIBER INTERACTIONS WITH ADDITIVES

System Number	Polymer Concentration, ppm		Time at 585 rpm, min	Degree of Fiber Flocculation
		Cationic Polymer		
A. No $LaCl_3$ — pH 7.0				
4-60-1	0.0		0	1.12
4-60-1	40.0		5	2.02
4-60-3	40.0		10	2.05
4-60-4	40.0		15	1.96
4-60-5	40.0		20	1.89
4-60-6	40.0		25	2.04
4-60-7	40.0		30	2.02
4-60-8	40.0		35	1.91
4-61-1	40.0		40	1.88
4-61-2	40.0		45	2.20
B. With $LaCl_3$ — pH 5.0				
4-66-1	0.0	no $LaCl_3$	0	1.11
4-66-2	0.0	with $LaCl_3$	0	1.68
4-66-3	1.0		5	2.10
4-67-1	1.0		10	2.27
4-67-2	1.0		15	2.21
4-67-3	1.0		20	2.30
4-67-4	1.0		25	2.18
4-67-5	1.0		30	2.15
		Anionic Polymer		
A. No $LaCl_3$ — pH 7.0				
4-62-3	0.0		0	1.22
4-62-4	25.0		5	1.71
4-62-5	25.0		10	1.77
4-63-1	25.0		15	1.63
4-63-2	25.0		20	1.63
4-63-3	25.0		25	1.71
4-63-4	25.0		30	1.71
4-63-5	25.0		35	1.75
4-63-6	25.0		40	1.72
4-63-7	25.0		45	1.70

TABLE XXI (Continued)

TIME OF AGITATION DATA ON FIBER-TO-FIBER INTERACTIONS WITH ADDITIVES

System Number	Polymer Concentration, ppm	Time at 585 rpm, min	Degree of Fiber Flocculation
B. With $LaCl_3$ — pH 9.0			
4-67-6	0.0 no $LaCl_3$	0	1.29
4-67-7	0.0 with $LaCl_3$	0	1.76
4-67-8	8.0	5	2.15
4-67-9	8.0	10	2.15
4-68-1	8.0	15	2.18
4-68-1	8.0	20	2.30
4-68-3	8.0	25	2.33
4-68-4	8.0	30	2.13
	Nonionic Polymer		
A. No $LaCl_3$ — pH 7.0			
4-64-1	0.0	0	1.23
4-64-2	25.0	5	1.32
4-64-3	25.0	10	1.34
4-64-4	25.0	15	1.26
4-64-5	25.0	20	1.34
4-64-6	25.0	25	1.30
4-64-7	25.0	30	1.24
4-64-8	25.0	35	1.34
4-64-9	25.0	40	1.30
4-64-10	25.0	45	1.35
B. With $LaCl_3$ — pH 9.0			
4-68-5	0.0 no $LaCl_3$	0	1.13
4-68-6	0.0 with $LaCl_3$	0	1.69
4-68-7	25.0	5	2.02
4-68-8	25.0	10	2.05
4-68-9	25.0	15	2.05
4-68-10	25.0	20	2.02
4-69-1	25.0	25	1.95
4-69-2	25.0	30	2.18

APPENDIX XV

EFFECTS OF ACCELERATED AGING ON FIBER-TO-FIBER INTERACTIONS

Two types of study were initiated to evaluate aging problems: (1) a sample aged by elevated temperature and (2) a sample aged at room temperature. One sample was placed at 110°C in a sealed container for 13 hours, then left at room temperature for 24 hours before evaluating with $LaCl_3$ at 585 rpm. Control runs of fresh fiber were made at the time the test sample was placed in the oven. The results of this study are given in Table XXII. It can be seen that no increase in the degree of coagulation was observed for the aged samples versus the controls. The 5×10^{-4}M concentration is well past the concentration required to compress and/or collapse the electric double layer as determined by earlier work in the current program.

Zeta-potential measurements were made on the test systems by Norm Colson of the Institute staff to determine if the added $LaCl_3$ was compressing the cellulose double layer. Samples were tested both with and without $LaCl_3$. Samples without electrolyte had zeta potentials of -22.5 to -25.0 millivolts with an average of -23.8 millivolts. Samples with electrolyte had zeta potentials of -2.3 to -10.2 millivolts with an average of -6.9 millivolts. These results indicated that the electrolyte was compressing the electric double layer, while the light probe measurements were not detecting any change in the degree of coagulation of the fibers.

The second aging test consisted of placing a sample of test fibers in a sealed container at room temperature for 12 days before evaluating with $LaCl_3$ at 585 rpm. Control runs were evaluated at the time the test fibers

were placed at room temperature. The results of this study are presented in Table XXIII. It is seen that the room temperature aging did not affect the degree of fiber cluster formation to any extent.

TABLE XXII

ELEVATED TEMPERATURE STUDY

System Number	Degree of Fiber Coagulation	Electrolyte Concentration, M
Controls		
3-24-1	0.46	--
3-24-1	0.51	1×10^{-6}
3-25-1	0.48	5×10^{-4}
Aged Samples		
3-27-7	0.54	--
3-27-8	0.53	1×10^{-6}
3-27-9	0.52	5×10^{-4}

TABLE XXIII

ROOM TEMPERATURE STUDY

System Number	Degree of Fiber Coagulation	Average	Electrolyte Concentration, M
Controls			
3-24-1	0.46	0.46	--
3-24-2	0.51	0.51	1×10^{-6}
3-25-1	0.48	0.48	5×10^{-4}
Aged Samples			
3-30-1	0.33	0.39 ± 0.08	--
3-30-4	0.45	± 22%	
3-30-2	0.35	0.39 ± 0.04	1×10^{-6}
3-30-5	0.43	± 10%	
3-30-3	0.52	0.53 ± 0.01	5×10^{-4}
3-30-6	0.54	± 1.9%	

APPENDIX XVI

POLYMER ADSORPTION BY CELLULOSE FIBERS

The data given below are for the amounts of the three polymers adsorbed by the cellulose fibers. Cationic systems were tested at pH 5.0, anionic at pH 9.0, and nonionic at pH 9.0.

System Number	System Description	Nitrogen, %		
		Test 1	Test 2	Average
--	Cationic polyacrylamide	13.92	13.50	13.71
--	Anionic polyacrylamide	13.87	13.94	13.90
--	Nonionic polyacrylamide	16.27	16.12	16.20
4-71-1	Background 255 rpm	0.013	0.006	0.009
4-71-2	40 ppm Cationic 255 rpm	0.078	0.070	0.074
4-71-3	100 ppm Cationic 255 rpm	0.100	0.106	0.103
4-71-4	200 ppm Cationic 255 rpm	0.121	0.108	0.114
4-72-1	10 ppm Cationic 585 rpm	0.028	0.027	0.027
4-72-2	50 ppm Cationic 585 rpm	0.088	0.094	0.091
4-72-3	100 ppm Cationic 585 rpm	0.103	0.099	0.101
4-72-4	30 ppm Anionic 585 rpm	0.013	0.013	0.013
4-72-5	60 ppm Anionic 585 rpm	0.009	0.009	0.009
4-72-6	120 ppm Anionic 585 rpm	0.008	0.013	0.010
4-73-1	30 ppm Anionic 255 rpm	0.011	0.008	0.009
4-73-2	60 ppm Anionic 255 rpm	0.010	0.007	0.009
4-73-3	120 ppm Anionic 255 rpm	0.010	0.014	0.012
4-73-4	30 ppm Nonionic 585 rpm	0.008	0.007	0.008
4-73-5	60 ppm Nonionic 585 rpm	0.006	0.007	0.007
4-73-6	120 ppm Nonionic 585 rpm	0.010	0.007	0.009
4-73-7	30 ppm Nonionic 255 rpm	0.008	0.009	0.009
4-73-8	60 ppm Nonionic 255 rpm	0.006	0.008	0.007
4-73-9	120 ppm Nonionic 255 rpm	0.010	0.007	0.008

All anionic and nonionic values are in the range of the background value, and any adsorption is less than the sensitivity of the measurement (0.01 of 1.0%). The cationic systems tabulated as gram of polymer per gram of fiber are presented in Table XXIV.

TABLE XXIV

CATIONIC POLYMER ADSORPTION BY CELLULOSE FIBER

System Number	Polymer Adsorbed, g/g fiber
4-71-2	4.74×10^{-3}
4-71-3	6.86×10^{-3}
4-71-4	7.66×10^{-3}
4-72-1	1.73×10^{-3}
4-72-2	5.83×10^{-3}
4-72-3	6.73×10^{-3}

It was desired to determine the coverage of polymer at monolayer coverage and so a Langmuir-type plot was constructed and is presented in Fig. 32. The slope of the curve obtained is the reciprocal of the monolayer coverage in grams of polymer per gram of fiber. The monolayer obtained was 9.0×10^{-3} g of polymer per gram of fiber. In order to obtain the area of polymer coverage per polymer unit, the above polymer coverage was divided into 10,000 cm^2/g of fiber, the fiber surface area. This value was then multiplied by 5×10^6 g/mole, the polymer molecular weight, followed by a division by Avogadro's number. The resultant value, 0.93×10^6 A^2/molecule, is the surface area of the fiber covered by a single polymer molecule at monolayer coverage.

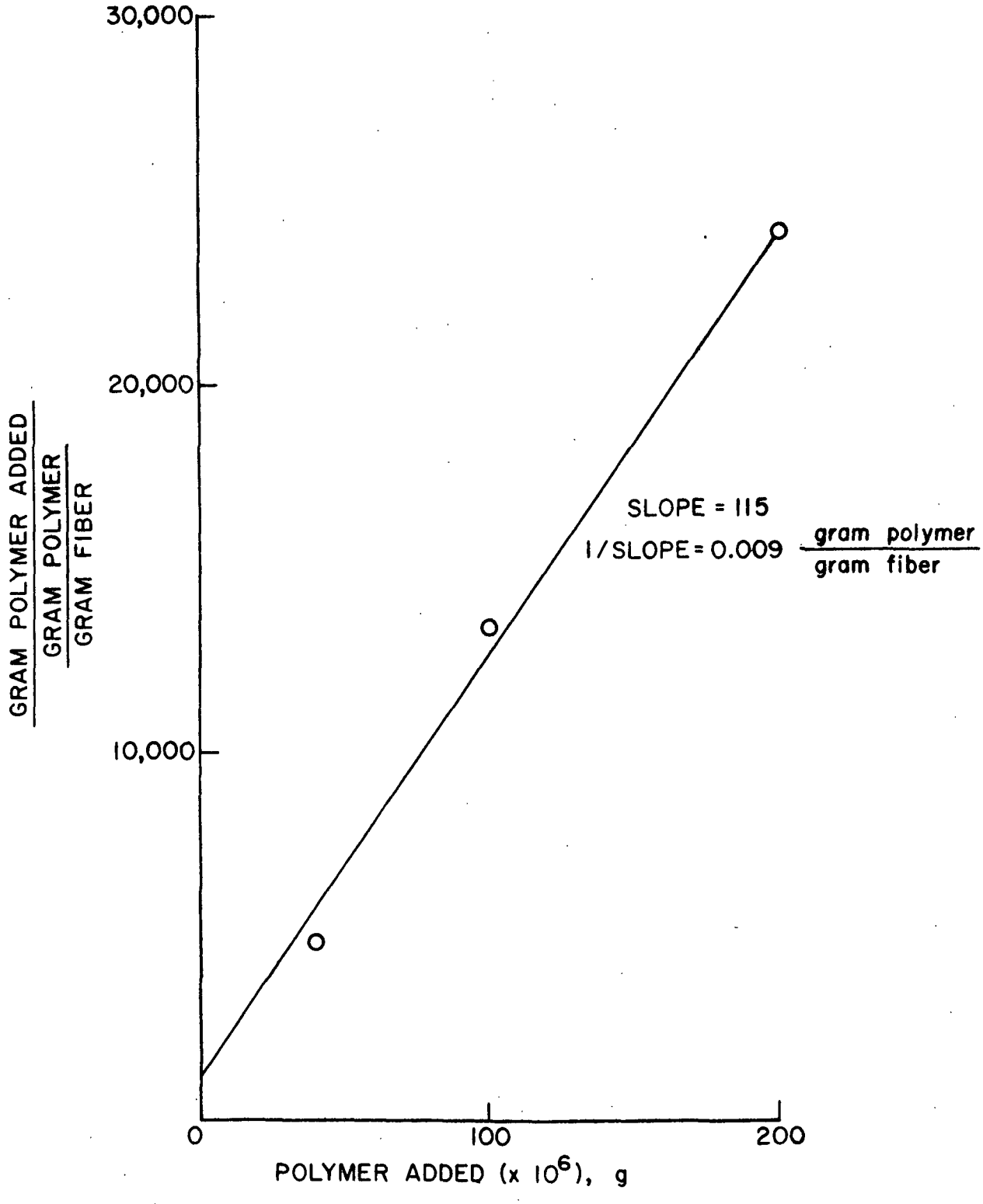


Figure 32. Langmuir Plot for Cationic Polymer Adsorption

APPENDIX XVII

EFFECTS OF POLYMER ON FIBER-TO-FIBER INTERACTIONS WITH FINES

The data presented in this appendix are for fiber-to-fiber interactions in the presence of fines as influenced by the three test polymers at pH 5 and 9 for both 255 and 585 rpm.

CATIONIC POLYMER

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation
A. pH 5; 255 RPM		
4-3-7	0.0	1.30
4-50-1	10.0	1.60
4-3-8	20.0	1.69
4-4-1	30.0	1.72
4-4-2	40.0	1.54
4-4-3	50.0	1.31
B. pH 9; 255 RPM		
4-58-1	10.0	1.59
A. pH 5; 585 RPM		
3-95-1	0.0	0.30
3-95-2	5.0	0.63
3-98-1	10.0	0.87
3-98-2	20.0	0.79
3-98-3	30.0	0.40
4-19-3	40.0	0.34
B. pH 9; 585 RPM		
4-1-1	0.0	0.39
4-1-2	5.0	0.83
4-2-1	10.0	0.93
4-2-2	20.0	0.75
4-2-3	30.0	0.48
4-21-2	50.0	0.39

ANIONIC POLYMER

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation
A. pH 5; 255 RPM		
4-28-1	0.0	1.11
4-28-2	10.0	1.29
4-28-3	30.0	1.60
4-28-4	50.0	1.19
B. pH 9; 255 RPM		
4-29-1	0.0	1.21
4-29-2	10.0	1.40
4-29-3	30.0	1.56
4-29-4	50.0	1.34
A. pH 5; 585 RPM		
4-11-1	0.0	0.47
4-11-2	10.0	0.51
4-11-3	20.0	0.65
4-12-1	30.0	0.63
4-12-2	40.0	0.47
4-26-1	50.0	0.60
B. pH 9; 585 RPM		
4-1-1	0.0	0.39
4-27-1	10.0	0.50
4-27-2	30.0	0.49
4-27-3	50.0	0.47

NONIONIC POLYMER

A. pH 5; 255 RPM		
4-28-1	0.0	1.11
4-33-1	10.0	1.29
4-33-2	30.0	1.60
4-34-1	50.0	1.09

System Number	Polymer Concentration, ppm	Degree of Fiber Flocculation
B. pH 9; 255 RPM		
4-29-1	0.0	1.21
4-34-2	10.0	1.38
4-34-3	30.0	1.62
4-35-1	50.0	1.04
A. pH 5; 585 RPM		
4-11-1	0.0	0.47
4-30-2	10.0	0.41
4-30-3	30.0	0.41
4-31-1	50.0	0.42
B. pH 9; 585 RPM		
4-1-1	0.0	0.39
4-31-2	10.0	0.36
4-31-3	30.0	0.46
4-32-1	50.0	0.44

APPENDIX XVIII

POLYMER PLUS $LaCl_3$ ELECTROLYTE EFFECTS ON FIBER-TO-FIBER INTERACTIONS WITH FINES

The data presented in this appendix are for fiber-to-fiber interactions in the presence of fines as influenced by the three test polymers and $LaCl_3$ electrolyte. Systems were evaluated at pH 5 and 9 for both 255 and 585 rpm.

NO ADDITIVES

System Number	Degree of Fiber Cluster Formation	Average
	255 rpm; pH 5 and 9	
4-39-4	1.16	1.18 ± 0.08
4-40-1	1.26	± 6.6%
4-41-2	1.08	
4-53-3	1.22	
4-47-4	1.20	
	585 rpm; pH 5 and 9	
4-36-1	0.28	0.31 ± 0.04
4-37-3	0.30	± 12%
4-51-4	0.35	

CATIONIC POLYMER

System Number	Polymer Concentration, ppm	Degree of Fiber Cluster Formation
A. pH 5; 255 RPM		
4-40-2	0.0	1.66
4-47-4	0.0	1.66
4-40-3	1.0	2.03
4-39-4	2.0	1.60
4-41-1	6.0	1.41

System Number	Polymer Concentration, ppm	Degree of Fiber Cluster Formation
B. pH 9; 255 RPM		
4-41-3	0.0	1.65
4-41-4	1.0	2.22
4-41-5	2.0	1.79
4-42-1	6.0	1.44
A. pH 5; 585 RPM		
4-45-2	0.0	0.61
4-36-3	2.0	0.67
4-37-1	4.0	0.64
4-37-213	8.0	0.59
B. pH 9; 585 RPM		
4-52-1	0.0	0.56
4-38-1	2.0	0.83
4-38-2	4.0	0.69
4-38-3	8.0	0.47
	ANIONIC POLYMER	
A. pH 5; 255 RPM		
4-40-2	0.0	1.66
4-47-4	0.0	1.66
4-48-1	2.0	1.75
4-48-2	6.0	2.02
4-49-1	10.0	1.45
4-62-1	15.0	1.19
B. pH 9; 255 RPM		
4-53-4	0.0	1.58
4-49-2	2.0	1.59
4-49-3	6.0	2.16
4-50-1	10.0	1.48
4-62-2	15.0	1.11

System Number	Polymer Concentration, ppm	Degree of Fiber Cluster Formation
A. pH 5; 585 RPM		
4-45-2	0.0	0.61
4-46-1	4.0	0.66
4-46-2	10.0	0.59
B. pH 9; 585 RPM		
4-52-1	0.0	0.56
4-46-4	4.0	0.65
4-47-1	10.0	0.59
	NONIONIC POLYMER	
A. pH 5; 255 RPM		
4-47-4	0.0	1.66
4-52-5	10.0	1.79
4-53-1	30.0	1.99
4-53-2	50.0	1.60
4-63-8	60.0	1.57
B. pH 9; 255 RPM		
4-53-4	0.0	1.58
4-53-5	10.0	1.94
4-54-1	30.0	1.74
4-54-2	50.0	1.62
4-63-9	60.0	1.46
A. pH 5; 585 RPM		
4-45-2	0.0	0.61
4-51-1	4.0	0.51
4-51-2	8.0	0.56
4-51-3	20.0	0.48
B. pH 9; 585 RPM		
4-52-1	0.0	0.56
4-52-2	4.0	0.55
4-52-3	8.0	0.54
4-52-4	20.0	0.57

APPENDIX XIX

EFFECTS OF POLYMERS ON FINES RETENTION

The data presented in this appendix are for the cationic, anionic, and nonionic polymer influences on fines retention at 255 and 585 rpm for pH values of 5 and 9.

CATIONIC POLYMER

System Number	Polymer Concentration, ppm	Fines Retention, %
A. pH 5; 255 RPM		
4-40-1	0.0	41.6
4-59-1	10.0	95.0
4-22-2	30.0	98.0
4-22-3	50.0	97.8
4-23-1	70.0	95.9
4-23-2	100.0	95.7
B. pH 9; 255 RPM		
4-29-1	0.0	43.7
4-58-1	10.0	81.1
4-24-1	50.0	98.1
4-24-2	90.0	93.6
4-24-3	120.0	96.4
A. pH 5; 585 RPM		
4-45-1	0.0	18.6
4-58-2	10.0	88.1
4-19-1	20.0	91.8
4-19-2	30.0	98.0
4-19-3	40.0	94.8
4-20-1	70.0	95.6
B. pH 9; 585 RPM		
4-31-3	0.0	20.8
4-59-1	10.0	57.9
4-21-1	30.0	96.9
4-21-2	50.0	95.9
4-21-1	70.0	95.5
4-22-1	90.0	93.6

ANIONIC POLYMER

System Number	Polymer Concentration, ppm	Fines Retention, %
A. pH 5; 255 RPM		
4-28-1	0.0	40.9
4-28-2	10.0	43.5
4-28-3	30.0	51.5
4-28-4	50.0	57.6
B. pH 9; 255 RPM		
4-29-1	0.0	43.7
4-29-2	10.0	48.5
4-29-3	30.0	60.5
4-29-4	50.0	61.9
A. pH 5; 585 RPM		
4-25-2	0.0	28.4
4-25-1	10.0	33.1
4-25-2	30.0	28.3
4-26-1	50.0	27.1
B. pH 9; 585 RPM		
4-27-1	0.0	24.2
4-27-1	10.0	23.2
4-27-2	30.0	28.4
4-27-3	50.0	31.1

NONIONIC POLYMER

A. pH 5; 255 RPM		
4-28-2	0.0	40.9
4-33-1	10.0	50.2
4-33-2	30.0	49.4
4-34-1	50.0	56.3
B. pH 9; 255 RPM		
4-34-2	0.0	45.7
4-34-2	10.0	48.9
4-34-3	30.0	47.1
4-35-1	50.0	51.6

System Number	Polymer Concentration, ppm	Fines Retention, %
A. pH 5; 585 RPM		
4-26-1	0.0	22.6
4-30-2	10.0	26.1
4-30-3	30.0	27.3
4-31-1	50.0	21.6
B. pH 9; 585 RPM		
4-31-2	0.0	24.4
4-31-2	10.0	22.7
4-31-3	30.0	24.1
4-32-1	50.0	22.3

APPENDIX XX

EFFECT OF POLYMERS PLUS $LaCl_3$ ELECTROLYTE ON FINES RETENTION

The data presented in this appendix are for the effects of cationic, anionic, and nonionic test polymers plus $LaCl_3$ electrolyte on fines retention at 255 and 585 rpm for pH 5 and 9.

CATIONIC POLYMER

System Number	Polymer Concentration, ppm	Fines Retention, %
A. pH 5; 255 RPM		
4-40-1	0.0 no $LaCl_3$	41.6
4-40-2	0.0 with $LaCl_3$	80.1
4-40-3	1.0	92.4
4-39-4	2.0	92.8
4-41-1	6.0	92.3
B. pH 9; 255 RPM		
4-41-2	0.0 no $LaCl_3$	43.7
4-41-3	0.0 with $LaCl_3$	77.8
4-41-4	1.0	91.5
4-41-5	2.0	92.8
4-42-1	6.0	93.9
A. pH 5; 585 RPM		
4-36-1	0.0 no $LaCl_3$	19.7
4-36-2	0.0 with $LaCl_3$	51.3
4-36-3	2.0	74.6
4-37-1	4.0	78.6
4-37-2	8.0	80.8
4-59-2	15.0	80.3
B. pH 9; 585 RPM		
4-51-4	0.0 no $LaCl_3$	26.1
4-37-4	0.0 with $LaCl_3$	58.3
4-38-1	2.0	75.4
4-38-2	4.0	82.0
4-38-3	8.0	81.5
4-59-3	15.0	84.9

ANIONIC POLYMER

System Number	Polymer Concentration, ppm	Fines Retention, %
A. pH 5; 255 RPM		
4-47-3	0.0 no $LaCl_3$	48.9
4-47-4	0.0 with $LaCl_3$	82.6
4-48-1	2.0	82.4
4-48-2	6.0	86.0
4-49-1	10.0	81.2
4-62-1	15.0	50.7
B. pH 9; 255 RPM		
4-41-2	0.0 no $LaCl_3$	43.7
4-41-3	0.0 with $LaCl_3$	77.8
4-49-2	2.0	84.4
4-49-3	6.0	88.1
4-50-1	10.0	90.1
4-62-2	15.0	41.1
A. pH 5; 585 RPM		
4-45-1	0.0 no $LaCl_3$	18.6
4-45-2	0.0 with $LaCl_3$	47.2
4-46-1	4.0	57.7
4-46-2	10.0	58.8
4-46-3	20.0	62.3
B. pH 9; 585 RPM		
4-51-4	0.0 no $LaCl_3$	26.1
4-52-1	0.0 with $LaCl_3$	51.0
4-46-4	4.0	69.4
4-47-1	10.0	76.1
4-47-2	20.0	83.7

NONIONIC POLYMER

A. pH 5; 255 RPM		
4-40-1	0.0 no $LaCl_3$	41.6
4-40-2	0.0 with $LaCl_3$	80.1
4-52-5	10.0	83.6
4-53-1	30.0	85.5
4-53-2	50.0	82.2
4-63-8	60.0	83.3

System Number	Polymer Concentration, ppm		Fines Retention, %
B. pH 9; 255 RPM			
4-53-3	0.0	no $LaCl_3$	40.6
4-53-4	0.0	with $LaCl_3$	83.8
4-53-5	10.0		87.5
4-54-1	30.0		87.2
4-54-2	50.0		89.8
4-63-9	60.0		89.7
A. pH 5; 585 RPM			
4-45-1	0.0	no $LaCl_3$	18.6
4-45-2	0.0	with $LaCl_3$	47.2
4-51-1	4.0		57.1
4-51-2	8.0		58.8
4-51-3	20.0		61.2
B. pH 9; 585 RPM			
4-51-4	0.0	no $LaCl_3$	26.1
4-52-1	0.0	with $LaCl_3$	51.0
4-52-2	4.0		61.6
4-52-3	8.0		63.5
4-52-4	20.0		66.3

APPENDIX XXI

EFFECT OF AGITATION TIME ON FINES RETENTION

System Number	Time at 585 rpm with Polymer, min	Fines Retention, %
	No $LaCl_3$	
A. 40 ppm Cationic Polymer		
4-60-1	0	63.6
4-60-2	5	98.4
4-60-3	10	97.8
4-60-4	15	97.2
4-60-5	20	Test failure
4-60-6	25	96.5
4-60-7	30	96.4
4-60-8	35	95.5
4-61-1	40	95.4
4-61-2	45	95.6
B. 25 ppm Anionic Polymer		
4-62-3	0	65.3
4-62-4	5	67.4
4-62-5	10	66.4
4-63-1	15	65.6
4-63-2	20	64.6
4-63-3	25	62.6
4-63-4	30	64.2
4-63-5	35	65.0
4-63-6	40	64.6
4-63-7	45	66.4
C. 25 ppm Nonionic Polymer		
4-64-1	0	63.9
4-64-2	5	62.1
4-64-3	10	62.0
4-64-4	15	60.3
4-64-5	20	59.6
4-64-6	25	59.3
4-64-7	30	62.1
4-64-8	35	60.8
4-64-9	40	62.1
4-64-10	45	61.8

System Number	Time at 585 rpm with Polymer, min	Fines Retention, %
	With $LaCl_3$	
A. 1 ppm Cationic Polymer		
4-66-1	0	54.5
4-66-2	0	85.1
4-66-3	5	94.1
4-67-1	10	93.1
4-67-2	15	92.5
4-67-3	20	91.4
4-67-4	25	91.9
4-67-5	30	91.0
B. 8 ppm Anionic Polymer		
4-67-6	0	56.8
4-67-7	0	85.1
4-67-8	5	94.1
4-67-9	10	93.1
4-68-1	15	92.5
4-68-2	20	91.4
4-68-3	25	91.9
4-68-4	30	91.0
C. 25 ppm Nonionic Polymer		
4-68-5	0	59.4
4-68-6	0	89.0
4-68-7	5	92.6
4-68-8	10	91.6
4-68-9	15	91.4
4-68-10	20	90.1
4-69-1	25	90.5
4-69-2	30	89.7

VITA

C. A. (Kasy) King

The author was born in Covington, Virginia on August 19, 1947. He spent most of his early years in Princeton, West Virginia, where he attended elementary, as well as junior and senior high school. During his years in Princeton, the author was active in the church, in organized baseball, and in school activities.

In June, 1970 the author received the degree of Bachelor of Science in Chemistry from Virginia Polytechnic Institute and State University. While at Virginia Tech he was a member of the Cooperative Education Program, working with the National Aeronautics and Space Administration at Huntsville, Alabama. During his stay in Huntsville, the author worked in a physical calibration laboratory, calibrating pressure gages and torque wrenches, as well as in a research laboratory, where he worked in the area of high temperature adhesives.

The author entered the Master of Science program in Surface Chemistry at Virginia Polytechnic Institute and State University in July, 1970, graduating from the program in June, 1972. He entered the Doctor of Philosophy program at The Institute of Paper Chemistry in September, 1972.

The author is a member of TAPPI, the Technical Association of the Pulp and Paper Industry.